Tris(pyrazolyl)phosphines and their Copper(I) Complexes

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Chapter 2

Tris(pyrazolyl)phosphine Oxides. Synthesis and Coordination Chemistry with Copper(I)

A set of substituted tris(pyrazolyl)phosphine oxides ($OP(Pz^x)_3$) has been prepared in high yield and applied as neutral scorpion-type ligands. The P-apex provides a convenient spectroscopic handle. Substitution at the 3-position of the pyrazolyl ring influences the steric demands of the ligand, while substitution at the 5-position enhances the stability. Copper(I) acetonitrile complexes of the $OP(Pz^x)_3$ ligands were prepared and tested in ligand exchange reactions with PPh_3 and CO. The ν(CO) values of the carbonyl complexes demonstrate the electron-withdrawing properties of the ligands. These observations show that $OP(Pz^x)_3$ ligands are an interesting extension of the widely used scorpion-type ligands.

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2.1 Introduction

Tris(pyrazolyl)methane (**A**, figure 2.1) is a versatile ligand that complexes with group 1–14 metals.[1,2] Several of these complexes are potent catalysts for reactions such as olefin polymerization,[3] carbene transfer,[4] and alkane oxidation.[5] An important feature of the tris(pyrazolyl)methane ligand is the possibility to adapt the steric and electronic properties by selecting the proper substituents. This versatility is shared with the established anionic tris(pyrazolyl)borate analogue, developed and termed the scorpionate ligand by Trofimenko.[6-9] For these tris(pyrazolyl)borates it was shown that increased steric bulk at the pyrazolyl 3-positions (as in **B**) can prevent disproportionation and stabilize half-sandwich complexes with open coordination sites available for further reactivity.[10,11] Moreover, strongly electron-withdrawing pyrazolyl substituents provide scorpionate ligands (such as **C**), whose metal complexes can display enhanced catalytic activity: e.g. in carbene transfer reactions.[12-14]

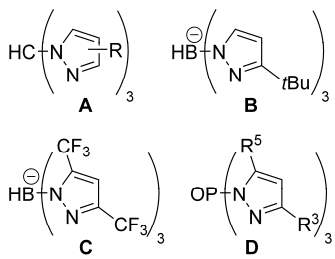


Figure 2.1. Selection of tris(pyrazolyl)-based ligands.

For tris(pyrazolyl)methane the substituent effect has not been fully exploited, probably due to the limited accessibility of these neutral scorpion-type ligands. While the synthetic protocols for preparing derivatized tris(pyrazolyl)methanes have been improved greatly at the beginning of this century, they remain far from ideal, especially for the more bulky substituted ligands. For example, a yield of only 43.7% was reported for the methane analogue of **B** and isolation required several purification steps.[15] Therefore, alternative neutral scorpion-type ligands are desired, but these are scarce and concern only the heavier tris(pyrazolyl)silane[16-19]

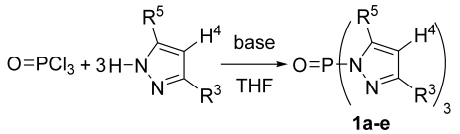
and the phosphorus-centered analogues (**D**). Peterson and co-workers were the first to report the isolation of both tris(pyrazolyl)phosphine ($P(Pz)_3$)[20] and the corresponding phosphine oxide ($OP(Pz)_3$).[21] Their work on the metal complexes of these ligands[22,23] was extended by Joshi et al.[24] with a single example and by the group of Tolman, who in a series of papers focused on the phosphine-oxide apex in C_3-chiral ligands containing chiral pyrazolyl groups.[25-28] The latest report on tris(pyrazolyl)phosphorus ligands was by the group of Ward, who used pyridyl substituted pyrazolyl rings to obtain a phosphine sulfide with possible κ^6-binding.[29] The potential applicability of phosphorus-centered tris(pyrazolyl) ligands is evident from these studies. However, they did not provide a systematic study that would facilitate the evaluation of the ligand properties relative to those of other scorpion-type ligands.

Here we report on the facile synthesis of a series of tris(pyrazolyl)phosphine oxides with increasing bulk near the binding pocket and their copper(I) acetonitrile complexes, as well as substitution reactions of these complexes with PPh_3 and CO. IR spectroscopy of the resulting CO complexes demonstrates the interesting electronic characteristics of these ligands.

2.2 Results and discussion

We selected the PO analogues **D** of three key tris(pyrazolyl)methane ligands to study the effects of a change in apex. $OP(3,5\text{-}Me_2Pz)_3$ (**1a**)[24] was chosen for direct comparison with its frequently used tris(pyrazolyl)methane analogue $HC(3,5\text{-}Me_2Pz)_3$. $OP(3\text{-}PhPz)_3$ (**1b**) and $OP(3\text{-}t\text{Bu}Pz)_3$ (**1c**)[25] represent ligands with increasing bulk in the proximity of the metal binding pocket; their borate analogues have been successfully applied in catalysis.[30-33] All three tris(pyrazolyl)phosphine oxides are readily prepared by addition of a phosphoryl trichloride solution to an ice-cold solution of 3 equiv of the appropriate pyrazole and a slight excess (3.1 equiv) of triethylamine in THF (Scheme 2.1); for **1a** the best results were obtained when phosphoryl trichloride was also present in excess (1.1 eq). After the reaction mixture was refluxed for several hours, the triethylammonium salts were filtered off. Removal of all volatiles, (for **1a** 8 h at 45 °C under high vacuum), gave the ligands as colorless or slightly yellow (**1b**) solids in high yields (**1a**, 90%; **1b**, 86%; **1c**, 93%).[34]

^{1}H and ^{13}C NMR spectra show a single set of signals for the pyrazolyl rings, which indicates the attachment of all rings to the apex with their substituent in the same position. This is in contrast with the initial outcome of the coupling reaction for the methane analogues that need an additional rearrangement step using *p*-toluenesulfonic acid to obtain the C_3-symmetric ligands.[15] The NMR resonances for 4-H and all ring carbons show coupling with phosphorus ($^{4}J_{H,P}$ = 3.6 – 3.8 Hz). The appearance of the ^{31}P NMR signal (δ −10.7 (**1a**), −14.8 (**1b**), and −14.4 (**1c**)) during the reaction proved to be an excellent tool to follow its progress.[35]

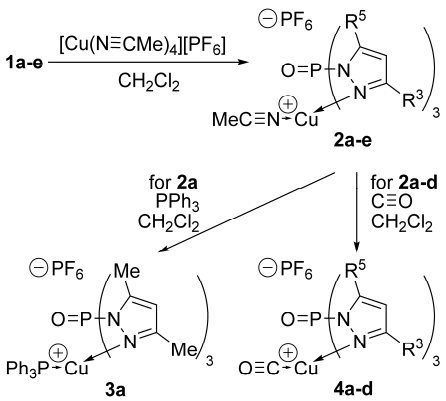


	1a	1b	1c	1d	1e
R^3 =	Me	Ph	*t*Bu	Ph	*t*Bu
R^5 =	Me	H	H	Me	Me
base =	Et_3N	Et_3N	Et_3N	KO*t*Bu	KO*t*Bu

Scheme 2.1. Syntheses of the tris(pyrazolyl)phosphine oxide ligands **1a**–**e**.

While **1b**,**c** are sensitive to moisture and decompose upon exposure to air, liberating the corresponding pyrazole, a $CDCl_3$ solution of **1a** can be treated with water without any noticeable change in the NMR spectra. We were curious whether the presence of the methyl groups at the 5-position of the pyrazolyl rings in **1a** caused this enhanced stability. Therefore, OP(3-Ph-5-MePz)$_3$ (**1d**) and OP(3-*t*Bu-5-MePz)$_3$ (**1e**) were prepared (Scheme 2.1), which are the methylated analogues of **1b**,**c**. A slight excess of phosphoryl trichloride (1.1 equiv) in THF was added slowly to an ice-cold mixture of the corresponding pyrazole (3 equiv) and potassium *tert*-butoxide (3.1 – 3.2 equiv) in THF. After the reaction mixture of **1d** was stirred at 0 °C (for 2 h) and room temperature (for 1 h) and that of **1e** at 60 °C (for 20 h), followed by workup, extraction into CH_2Cl_2, removal of all volatiles, and column chromatographic purification, the desired ligands **1d** (30%, δ ^{31}P −10.3) and **1e** (53%, δ ^{31}P −10.5) were obtained as colorless solids. Exposure to air and addition of water to these methylated ligands did not show any degradation, thereby confirming that the methyl groups at the 5-position do indeed protect these ligands from hydrolysis.

As these PO scorpion-type ligands are readily accessible we were eager to explore their coordination chemistry. Copper(I) acetonitrile complexes were prepared from **1a–e** by allowing a 1 : 1 mixture of the ligand and $[Cu(NCMe)_4][PF_6]$ to react in CH_2Cl_2 at room temperature (Scheme 2.2). The reaction with **1a** gave, after stirring for 30 min, concentration, and crystallization/precipitation by addition of pentane, the desired complex $[OP(3,5\text{-}Me_2Pz)_3Cu(NCMe)][PF_6]$ (**2a**) in 91% yield (δ ^{31}P −19.8, −144.4 (septet, $^1J_{P,F}$ = 711 Hz, PF_6)). Likewise, stirring the reaction mixtures of **1b–e** for 2 h, removing all volatiles, washing the residue with MTBE, and drying at 70 °C gave excellent yields of $[OP(3\text{-}PhPz)_3Cu(NCMe)][PF_6]$ (**2b**, 87%, δ ^{31}P −19.8), $[OP(3\text{-}t\text{BuPz})_3Cu(NCMe)][PF_6]$ (**2c**, 85%, δ ^{31}P −20.7), $[OP(3\text{-}Ph\text{-}5\text{-}MePz)_3Cu(NCMe)][PF_6]$ (**2d**, 98%, δ ^{31}P −18.0), and $[OP(3\text{-}t\text{Bu}\text{-}5\text{-}MePz)_3Cu(NCMe)][PF_6]$ (**2e**, 96%, δ ^{31}P −17.1). Also for these reactions ^{31}P NMR spectroscopy proved to be an invaluable diagnostic tool as upfield shifts of 5–8 ppm were observed for the PO apex upon complexation. A single set of ^{1}H and ^{13}C NMR signals was observed for the pyrazolyl rings of all complexes, suggesting κ^3-coordination of the ligands in analogy to the reported CH analogues of complexes **2a–c**.[36] Crystal structure determinations of **2c**,**d** (Figure 2.1, Table 2.1) confirmed this coordination mode. Both molecular structures display a distorted tetrahedral geometry around copper. The Cu–$N^{pyrazolyl}$ distance for **2c** ranges between 2.089(2) and 2.134(2) Å, while the Cu–$N^{acetonitrile}$ distance is shorter (1.911(2) Å). The N–Cu–N angles between the pyrazolyl rings range from 90.16(8) to 94.24(8)° and those between acetonitrile and the pyrazolyl donors range from



Scheme 2.2. Preparation and reactivity of the Cu(I) complexes **2a**–**e**.

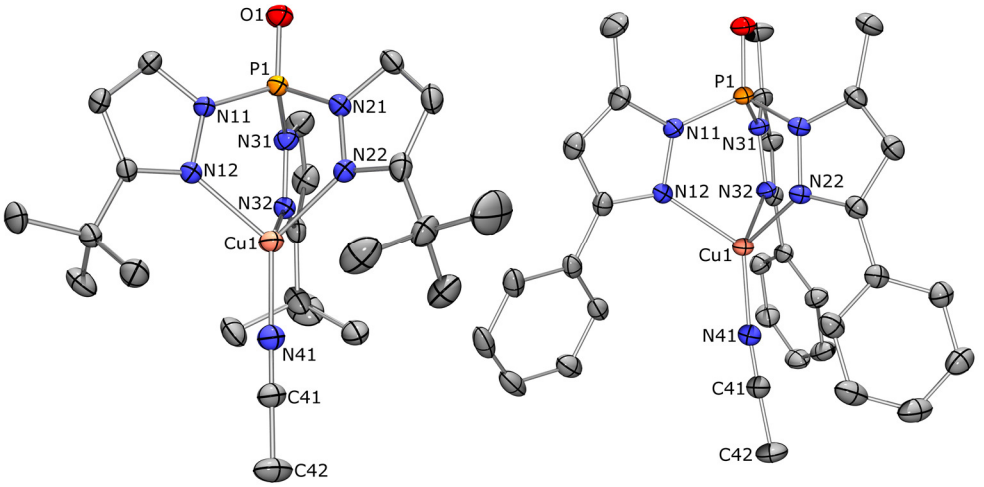


Figure 2.1. Displacement ellipsoid plot of **2c** (left) and **2d** (right) drawn at the 50% probability level. Hydrogen atoms, co-crystallized CH_2Cl_2 (for **2c**) and the PF_6 anion are omitted for clarity.

121.88(10) to 125.23(9)°. All these structural features compare very well with those of its CH analogue,[36] despite the significantly larger phosphorus atom at the apex of the ligand (P–N distances in **2c** from 1.670(2) to 1.675(2) Å, relative to C–N distances of 1.427(14) to 1.447(15) Å in [HC(3-*t*Bu-Pz)$_3$Cu(NCMe)][PF_6]). In **2d** all coordinating nitrogens are closer to the copper center than in **2c** (Cu–$N^{pyrazolyl}$ distances from 2.0709(14) to 2.0799 (14) Å, Cu–$N^{acetonitrile}$ distance: 1.8876(14) Å), while the angles around the copper are comparable (N–Cu–N angles between pyrazolyl rings 91.42(5) – 92.30(5)° and between acetonitrile and the pyrazolyl donors 121.47(6) – 128.13(6)°).

With this new set of tris(pyrazolyl)phosphine oxide complexes at hand and their structures established unequivocally, we were interested in their reactivity. To start, we investigated the ligand exchange reaction of **2a** with the σ-donor ligand PPh_3 which is very common in Cu(I) chemistry (Scheme 2.2). After 3 h, full conversion in CH_2Cl_2 was observed by ^{31}P NMR spectroscopy, which showed the PO scorpion-ligand as a sharp singlet at δ −20.2, while the broad signal of copper bound PPh_3 appeared at δ 6.8 (i.e. 12.1 ppm downfield relative to free PPh_3). Removal of all

Table 2.1. Selected Bond Distances and Angles for **2c**,**d**, **3a**, and [HC(3-*t*Bu-Pz)$_3$Cu(NCMe)][PF$_6$].

	2c	**2d**	**3a**	[HC(3-*t*Bu-Pz)$_3$ Cu(NCMe)][PF$_6$][a]
		Bond distances (Å)		
Cu1–N12	2.089(2)	2.0710(13)	2.0863(17)	2.138(9)
Cu1–N22	2.134(2)	2.0799(13)	2.0843(18)	2.122(9)
Cu1–N32	2.101(2)	2.0778(13)	2.1039(17)	2.061(9)
(Cu1–L)	(Cu1–N41)	(Cu1–N41)	(Cu1–P2)	(Cu1– N41)
Cu1–L	1.911(2)	1.8876(14)	2.1820(5)	1.873(9)
(A–N)	(P1–N)	(P1–N)	(P1–N)	(C1–N)
A–N11	1.675(2)	1.6828(14)	1.6808(18)	1.443(16)
A–N21	1.670(2)	1.6801(14)	1.6729(18)	1.447(15)
A–N31	1.672(2)	1.6889(14)	1.6781(18)	1.427(14)
		Bond angles (°)		
(N–Cu1–L)	(N–Cu1–N41)	(N–Cu1–N41)	(N–Cu1–P2)	(N–Cu1–N41)
N12–Cu1–L	125.23(9)	128.13(6)	126.45(5)	122.95(4)
N22–Cu1–L	121.88(10)	122.17(6)	125.39(5)	125.7(4)
N32–Cu1–L	122.70(9)	121.47(6)	122.77(5)	128.69(5)
N12–Cu1–N22	90.16(8)	92.30(5)	90.00(7)	89.0(4)
N12–Cu1–N32	93.90(8)	91.41(5)	89.74(7)	89.9(4)
N22–Cu1–N32	94.24(8)	91.69(5)	91.91(7)	88.8(4)
Cu1–N41–C41	176.6(2)	174.03(15)		174.1(14)

[a]Data taken from ref [36].

volatiles and washing with Et$_2$O gave the desired PPh$_3$ adduct **3a** as a colorless solid in 78% yield. The molecular structure of this complex (Figure 2.2, Table 2.1) shows again the copper center in a distorted tetrahedral surrounding with N–N angles between 89.74(7) and 91.91(7)° and P–N angles ranging from 122.77(5) to 126.45(5)°. The Cu–N distances fall in between those found for **2c**,**d** (i.e. from 2.0843(18) to 2.1039(17) Å); the Cu–P distance of 2.1820(5) Å is within the range found in related tris(pyrazolyl) copper complexes (from 2.1469(5) Å for C(3,5-Me$_2$Pz)$_3$Cu(PPh$_3$)[37] to 2.219(1) Å for HB(3,5-(CF$_3$)$_2$Pz)$_3$Cu(PPh$_3$)[38]).

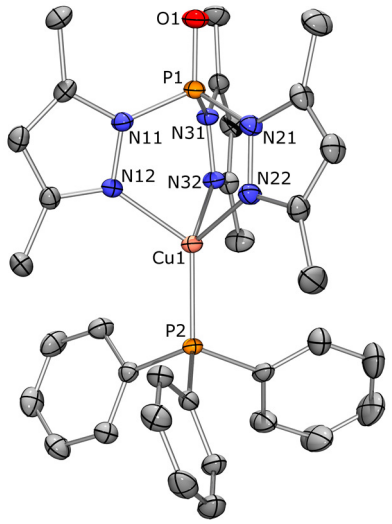


Figure 2.2. Displacement ellipsoid plot of **3a** drawn at the 50% probability level. Hydrogen atoms, co-crystallized CH_2Cl_2, and the PF_6 anion are omitted for clarity.

Having learned that ligand substitutions are feasible, we were eager to explore the reactivity of the Cu(I) complexes toward CO. Attachment of this well-known π-acceptor to a metal complex can provide insight into the electron density of the metal by virtue of determining its ν(CO) IR frequency. This, in turn, allows an evaluation of the effect of substituting the CH-apex for the PO-apex on the electronic properties of the scorpion ligand. Exposing CH_2Cl_2 solutions of all copper acetonitrile adducts **2a–e** to a CO atmosphere for a prolonged time, followed by precipitation on addition of pentane, gave mixed results (Scheme 2.2). While [OP(3-Ph-5-MePz)$_3$Cu(CO)][PF_6] (**4d**) was obtained quantitatively after stirring for 64 h at room temperature, **2e** showed no conversion at all.[39] The other complexes gave partial conversions after 1 month (**2a** : **4a**, 0.3 : 1.0; **2c** : **4c**, 4 : 1) while for [OP(3-PhPz)$_3$Cu(CO)][PF_6] (**4b**) (after 18 h) the ratio could not be determined due to overlap of the signals in the ^{1}H NMR spectrum. IR spectroscopy of all four CO complexes **4a–d** showed ν(CO) values that are at least 16 cm^{-1} higher than those for the analogous CH-centered complexes (Table 2.2). This shows that the π-back donation to CO is much lower in our complexes, thereby demonstrating a significant decrease in the electron density of the metal centers. When the ν(CO) frequencies of HB(3,5-Me$_2$Pz)$_3$Cu(CO) (2066

cm^{-1}),[40] $[HC(3,5\text{-}Me_2Pz)_3Cu(CO)][PF_6]$ (2113 cm^{-1}),[36] and **4a** (2129 cm^{-1}) are compared, it is clear that not only the charge of the ligand (the borate versus the last two), but also the nature of the apex (the methane versus the phosphine oxide **4a**, which are both neutral ligands) influences the electron density of the complexed metal. The CO stretching frequency of **4a** has the highest value of the complexes reported here. It approaches the 2137 cm^{-1} reported for the scorpionate copper(I) complex with the very electron withdrawing $HB(3,5\text{-}(CF_3)_2Pz)_3$ ligand.[41] It has been demonstrated that the corresponding Ag complexes of this ligand benefit from the low electron density on the metal center in several catalytic reactions.[12] This holds promise for the performance of our readily accessible PO ligands in catalysis, which is under current investigation.

Table 2.2. Carbonyl Stretching Frequencies for Tris(pyrazolyl)phosphine Oxide- and Tris(pyrazolyl)methane Copper(I) Carbonyl Complexes.

	ν(CO) (cm^{-1})	Reference
$[OP(3,5\text{-}Me_2Pz)_3Cu(CO)][PF_6]$ (**4a**)	2129	this work
$[OP(3\text{-}PhPz)_3Cu(CO)][PF_6]$ (**4b**)	2121	this work
$[OP(3\text{-}tBuPz)_3Cu(CO)][PF_6]$ (**4c**)	2118	this work
$[OP(3\text{-}Ph\text{-}5\text{-}MePz)_3Cu(CO)][PF_6]$ (**4d**)	2111	this work
$[HC(3,5\text{-}Me_2Pz)_3Cu(CO)][PF_6]$	2113	[36]
$[HC(3\text{-}PhPz)_3Cu(CO)][PF_6]$	2104	[36]
$[HC(3\text{-}t\text{BuPz})_3Cu(CO)][PF_6]$	2100	[36]

2.3 Conclusions

We have expanded the scope of a highly accessible neutral class of scorpion-type ligands. These tris(pyrazolyl)phosphine oxides are readily obtained in good yields. Their phosphorus apex provides a convenient spectroscopic handle to monitor the ligand synthesis and the fate of the ligand in complexation reactions and follow up chemistry. We have shown that these ligands are suitable to support Cu(I) complexes with different ancillary ligands and have probed the CO stretching frequency of their CO adducts. This showed the tris(pyrazolyl)phosphine oxides to be on the low-donating side of the whole range of scorpion-type ligands,[12] which makes exploring their behavior in catalysis highly interesting.

2.4 Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. 3-Phenylpyrazole,[11] 3-*tert*-butylpyrazole,[11] 3-methyl-5-phenylpyrazole,[42] 5,5-dimethylhexane-2,4-dione,[43] and tetrakis(acetonitrile)copper(I) hexafluorophosphate[44] were prepared according to literature procedures. Triethylamine was dried over sodium and phosphoryl trichloride was distilled under nitrogen before use. Other reagents were obtained commercially and used as received. NMR spectra were recorded on a Bruker Avance 250, a Bruker Avance 400 or on a Bruker Ultrashield 500 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent resonances ($CDCl_3$: ^{1}H, 7.26 ppm ($CHCl_3$), $^{13}C\{^{1}H\}$, 77.16 ppm; CD_2Cl_2: ^{1}H, 5.32 ppm ($CDHCl_2$), $^{13}C\{^{1}H\}$, 53.84 ppm;). Other nuclei were referenced to external standards: ^{19}F, $BF_3{\cdot}Et_2O$ (0 ppm); ^{31}P, 85% H_3PO_4 (0 ppm). IR spectra were recorded on a Shimadzu FTIR-84005 spectrophotometer, using the ATR technique. Peak intensities are marked as follows: s = strong, m = medium, w = weak. High-resolution electrospray ionization-mass spectrometry (HR ESI-MS) was performed using a Bruker MicroTOFQ, ESI in positive mode (capillary voltage 4.5 kV). Flash chromatography was performed using SiliaFlash® P60 (0.040–0.063 mm) silica gel with an overpressure of about 0.5 bar. Melting points were measured on samples in unsealed capillaries on a Stuart Scientific SMP3 melting point apparatus.

Preparation of 3-Methyl-5-tert-butylpyrazole. This compound was prepared following the procedure reported for 3-methyl-5-phenylpyrazole.[42] Hydrazine hydrate (1.75 mL, 35.0 mmol) was added dropwise to a solution of 5,5-dimethylhexane-2,4-dione (1.0 g, 7.0 mmol) in methanol (30 mL) at 0 °C. The reaction was slightly exothermic and had a yellow hue. After 1 h all volatiles were removed by rotary evaporation. The resulting solid was washed on a glass frit with *n*-hexane and fully dried *in vacuo*. 3-Methyl-5-*tert*-butylpyrazole was obtained as a colorless solid (0.99 g, 7.0 mmol, quantitative). ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.30 (s, 9H, CMe_3), 2.27 (s, 3H, 5-Me), 5.88 (s, 1H, 4-H); the signal for NH was not observed.

Preparation of Tris(3,5-dimethylpyrazolyl)phosphine Oxide (1a).[24] Phosphoryl trichloride (6.31 g, 41.1 mmol) in THF (30 mL) was added dropwise (0.5 h) to a stirred

solution of 3,5-dimethylpyrazole (11.05 g, 114.9 mmol) and triethylamine (16.6 mL, 120 mmol) in THF (100 mL) at 0 °C. During the addition a colorless solid was formed. After the addition was complete, the reaction mixture was warmed to room temperature and was refluxed for 3 h. After 1h the mixture became slightly yellow. After 3 h, the reaction mixture was filtered over silica and was washed with THF (3×15 mL). The combined filtrates were evaporated to dryness and pentane was added to the residue. This was also removed *in vacuo* to remove traces of solvent. Some byproducts remained, according to ^{1}H and ^{31}P NMR spectra, and were removed by sublimation under vacuum at 45 °C for 8 h. **1a** was obtained as a colorless solid (11.4 g, 34.3 mmol, 89.6%). Mp: 91–93 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 2.18 (s, 9H, Me), 2.29 (s, 9H, Me), 6.00 (d, 3H, $^{4}J_{H,P}$ = 3.8 Hz, Pz) ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 12.4 (s, Me), 14.1 (s, Me), 111.1 (d, $^{3}J_{C,P}$ = 8.1 Hz, Pz C-4), 148.2 (d, $^{2}J_{C,P}$ = 11.9 Hz, Pz C-5), 154.9 (d, $^{3}J_{C,P}$ = 15.7 Hz, Pz C-3). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −10.7. IR: ν 3109 (w), 2993 (w), 2962 (w), 2928 (w), 1577 (m), 1408 (m), 1373 (w), 1284 (s), 1176 (s), 1141 (s), 1084 (m), 1041 (w), 1022 (m), 960 (s), 848 (m), 806 (m), 767 (m), 632 (m), 594 (s), 582 (s), 563 (s), 505 (m), 486 (m), 459 (m), 439 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{15}H_{22}N_6OP$ (M + H) 333.1587, found 333.1572.

Preparation of Tris(3-phenylpyrazolyl)phosphine Oxide (1b). A solution of phosphoryl trichloride (1.82 g, 11.9 mmol) in THF (10 mL) was added over 30 min to a stirred solution of 3-phenylpyrazole (5.13 g, 35.6 mmol) and triethylamine (5.1 mL, 37 mmol) in THF (40 mL) at 0 °C. During the addition a colorless solid formed. After the addition the solution was allowed to attain room temperature, after which it was stirred overnight, refluxed for 4 h, stirred overnight again, and refluxed for 3 h more after which ^{31}P NMR showed the reaction to be complete. The reaction mixture was filtered with a filter cannula and washed with THF (2 × 10 mL). All volatiles were evaporated, and the residue was analyzed by ^{1}H NMR spectroscopy. As this showed the presence of some triethylammonium chloride, the solid was dissolved in THF and filtered over silica. The residue was washed with THF (2 × 10 mL), and all volatiles were removed from the combined filtrates. This afforded **1b** as a pale yellow solid (4.88 g, 10.2 mmol, 86.0%). Mp: 175–180 °C. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 6.85 (dd, 3H, $^{4}J_{H,P}$ = 3.6 Hz, $^{3}J_{H,H}$ = 2.8 Hz, Pz 4-H), 7.36–7.43 (m, 9H, $H_{meta,para}$), 7.86 (d, 6H, $^{3}J_{H,H}$ = 6.6 Hz, H_{ortho}), 8.01 (d, 3H, $^{3}J_{H,H}$ = 2.8 Hz, Pz 5-H). ^{13}C{^{1}H} NMR

(125.8 MHz, $CDCl_3$): δ 107.8 (d, $^3J_{C,P}$ = 7.2 Hz, Pz C-4), 126.8 (s, C_{ortho}), 128.9 (s, C_{meta}), 129.5 (s, C_{para}), 131.4 (s, C_{ipso}), 137.6 (d, $^2J_{C,P}$ = 12.1 Hz, Pz C-5), 159.1 (d, $^3J_{C,P}$ = 15.5 Hz, Pz C-3). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ −14.8. IR: ν 1535 (m), 1500 (w), 1450 (w), 1381 (w), 1327 (m), 1300 (m), 1280 (w), 1215 (m), 1161 (m), 1091 (m), 1072 (m), 1030 (s), 952 (m), 756 (s), 694 (s), 609 (s), 586 (s), 520 (m), 505 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{27}H_{22}N_6OP$ (M + H) 477.1587, found 477.1576.

Preparation of Tris(3-*tert*-butylpyrazolyl)phosphine Oxide (1c). [25] A solution of phosphoryl trichloride (1.95 g, 12.7 mmol) in THF (10 mL) was added over 30 min to a stirred solution of 3-*tert*-butylpyrazole (4.74 g, 38.2 mmol) and triethylamine (5.5 mL, 40 mmol) in THF (40 mL) at 0 °C. During the addition a colorless solid was formed. After the addition was complete, the reaction mixture was warmed to room temperature, stirred overnight, and refluxed for 4 h after which ^{31}P-NMR showed the reaction to be complete. All solids were removed by cannula filtration and the residue was washed with THF (2 × 10 mL). All volatiles were evaporated from the combined filtrates and pentane was added to the residue. This was also removed *in vacuo* to remove the last trace of solvent, affording **1c** as a colorless solid (4.94 g, 11.9 mmol, 93.4%). Mp: 150–153 °C. ^1H NMR (500.2 MHz, $CDCl_3$): δ 1.27 (s, 27H, CMe_3), 6.33 (dd, 3H, $^4J_{H,P}$ = 3.6 Hz, $^3J_{H,H}$ = 2.8 Hz, Pz 4-H), 7.65 (d, 3H, $^3J_{H,H}$ = 2.8 Hz, Pz 5-H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 30.0 (s, CMe_3), 32.8 (s, CMe_3), 107.0 (d, $^3J_{C,P}$ = 7.6 Hz, Pz C-4), 136.3 (d, $^2J_{C,P}$ = 12.0 Hz, Pz C-5), 169.4 (d, $^3J_{C,P}$ = 13.8 Hz, Pz C-3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −14.4. IR: ν 3113 (w), 2958 (w), 2904. (w), 2866 (w), 1535 (m), 1500 (m), 1481 (m), 1462 (w), 1381 (w), 1365 (m), 1323 (m), 1296 (m), 1230 (m), 1211 (m), 1176 (m), 1141 (s), 1103 (s), 1041 (s), 972 (w), 952 (m), 883 (w), 829 (w), 798 (w), 775 (s), 725 (w), 694 (w), 678 (w), 628 (s), 605 (s), 563 (s), 513 (w), 493 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{20}H_{34}N_6OP$ (M + H) 417.2526, found 417.2511.

Preparation of Tris(3-phenyl-5-methylpyrazolyl)phosphine Oxide (1d). A solution of phosphoryl trichloride (340 mg, 0.21 mL, 2.22 mmol) in THF (3 mL) was added dropwise to a solution of potassium *tert*-butyloxide (751 mg, 6.69 mmol) and 3-methyl-5-phenylpyrazole (1.00 g, 6.32 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h, followed by 1 h at room temperature. Water and CH_2Cl_2 were added, the organic phase was separated, and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over

$MgSO_4$ and concentrated under reduced pressure. Column chromatographic purification (SiO_2, pentane/ MTBE 10/5) gave **1d** (328 mg, 0.633 mmol, 30.0%) as a colorless solid. Mp: 169–171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.43 (s, 9H, Pz 5-Me), 6.61 (d, 3H, $^4J_{H,P}$ = 3.5 Hz, Pz 4-H), 7.30–7.37 (m, 9H, $H_{meta,para}$), 7.67 (d, 6H, $^3J_{H,H}$ = 6.8 Hz, H_{ortho}). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 12.5 (s, Pz 5-Me), 108.3 (d, $^3J_{C,P}$ = 7.6 Hz, Pz C-4), 126.5 (s, C_{ortho}), 128.7 (s, C_{meta}), 129.0 (s, C_{para}), 132.0 (s, C_{ipso}), 149.1 (d, $^2J_{C,P}$ = 11.8 Hz, Pz C-5), 156.7 (d, $^3J_{C,P}$ = 15.7 Hz, Pz C-3). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −10.3. IR: ν 3113 (w), 2963 (w), 1570 (w), 1462 (w), 1400 (w), 1280 (m), 1261 (m), 1165 (s), 1095 (m), 1076 (m), 1041 (m), 1022 (m), 991 (m), 941 (m), 918 (w), 821 (m), 798 (m), 767 (m), 736 (m), 694 (s), 651 (m), 590 (s), 547 (m), 528 (w), 501 (w), 482 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{30}H_{28}N_6OP$ (M + H) 519.2057, found 519.2043.

Preparation of Tris(3-*tert*-butyl-5-methylpyrazolyl)phosphine Oxide (1e). A solution of phosphoryl trichloride (982 mg, 0.60 mL, 6.40 mmol) in THF (8 mL) was added dropwise to a solution of potassium *tert*-butyloxide (2.02 g, 18.0 mmol) and 3-methyl-5-*tert*-butylpyrazole (2.39 g, 17.3 mmol) in THF (16 mL) at 0 °C. The mixture was then heated to 60 °C and stirred at this temperature for 20 h. After the mixture was cooled to ambient temperature, water and CH_2Cl_2 were added, and the mixture was filtered through Celite. The organic phase was separated, and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatographic purification (SiO_2, pentane/MTBE 10/4; iodine was used to visualize TLC spots) gave **1e** (1.41 g, 3.07 mmol, 53.3%) as a colorless solid. Mp: 107–109 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.18 (s, 27H, CMe_3), 2.19 (dd, $^4J_{H,H}$ = 0.9 Hz, $^4J_{H,P}$ = 0.5 Hz, 9H, Pz 5-Me), 6.04 (dd, 3H, $^4J_{H,P}$ = 3.8 Hz, $^4J_{H,H}$ = 0.9 Hz, Pz 4-H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 12.0 (s, Pz 5-Me), 29.9 (s, CMe_3), 32.6 (s, CMe_3), 107.7 (d, $^3J_{C,P}$ = 7.9 Hz, =CH), 147.9 (d, $^2J_{C,P}$ = 11.7 Hz, Pz C-3), 166.9 (d, $^3J_{C,P}$ = 14.5 Hz, Pz C-5). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ −10.5. IR: ν 2962 (w), 2928 (w), 2866 (w), 1573 (m), 1485 (w), 1458 (w), 1446 (w), 1404 (w), 1384 (w), 1361 (w), 1296 (s), 1234 (m), 1211 (w), 1165 (m), 1114 (w), 1099 (w), 1087 (w), 1068 (w), 960 (m), 802 (m), 725 (m), 636 (w), 594 (s), 578 (s), 536 (w), 513 (w) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{24}H_{40}N_6OP$ (M + H) 495.2996, found 459.2985.

Preparation of Copper(I) Acetonitrile Tris(3,5-dimethylpyrazolyl)phosphine Oxide Hexafluorophosphate (2a). Dichloromethane (5 mL) was added with stirring to a mixture of **1a** (175 mg, 0.527 mmol) and $[Cu(NCMe)_4][PF_6]$ (197 mg, 0.528 mmol). Within a few minutes a clear reaction mixture resulted that was stirred for 30 min. After concentration (~4 mL) pentane (0.5 mL) was added and after brief heating, the resulting clear solution was stored at −70 °C for crystallization yielding 119 mg (0.205 mmol) of colorless crystalline material after drying *in vacuo*. Treating the mother liquor with pentane (10 mL) resulted in a second batch of colorless powder (159 mg, 0.273 mmol) that was spectroscopically identical to the first batch. Total yield: 278 mg, 0.478 mmol, 90.6%. Mp: 230–233 °C dec. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 2.36 (s, 9H, 3-Me), 2.37 (s, 3H, N≡CMe), 2.58 (s, 9H, 5-Me), 6.10 (d, 3H, $^4J_{H,P}$ = 5.2, Pz 4-H). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 2.7 (N≡C*Me*), 13.7 (s, 5-Me), 14.0 (s, 3-Me), 110.8 (d, $^3J_{C,P}$ = 9.8 Hz, Pz C-4), 117.3 (s, N≡C), 149.8 (d, $^2J_{C,P}$ = 11.5 Hz, Pz C-5), 157.3 (d, $^3J_{C,P}$ = 11.4 Hz, Pz C-3). ^{19}F{^{1}H} NMR (235.4 MHz, $CDCl_3$): δ −73.6 (d, $^1J_{F,P}$ = 712 Hz). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −144.4 (septet, 1P, $^1J_{P,F}$ = 712 Hz, PF_6), −19.8 (s, 1P, PO). IR: ν 3148 (w), 3090 (w), 2970 (w), 1574 (w), 1531 (w), 1497 (w), 1458 (w), 1408 (w), 1373 (w), 1319 (m), 1273 (m), 1169 (m), 1095 (w), 1076 (w), 1038 (m), 972 (w), 922 (w), 829 (vs), 764 (s), 690 (m), 621 (m), 579 (s), 555 (s), 517 (m), 447 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{15}H_{21}CuN_6OP$ (M − PF_6 − CH_3CN) 395.0805, found 395.0781.

General Procedure for the Preparation of the Other Copper(I) Acetonitrile Complexes: Freshly deoxygenated dichloromethane was added to a mixture of the corresponding ligand (1.00 mmol) and $[Cu(NCMe)_4][PF_6]$ (1.00 mmol) at 20 °C. The resulting suspension was stirred at room temperature, which eventually gave a clear solution. After 2 h of stirring ^{31}P NMR indicated full conversion to the target complex. The solvent was evaporated and the solid washed with MTBE, filtered, and dried at 70 °C (in some cases a small solvent signal was still observed by NMR) to give the target complexes as colorless solids.

Copper(I) Acetonitrile Tris(3-phenylpyrazolyl)phosphine Oxide Hexafluorophosphate (2b). Yield: 87%. Mp: 202–205 °C. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 1.92 (s, 3H, N≡CMe), 6.94 (dd, 3H, $^4J_{H,P}$ = 4.5 Hz, $^3J_{H,H}$ = 2.9 Hz, Pz 4-H), 7.46–7.57 (m, 9H, $H_{meta,para}$), 7.78 (m, 6H, H_{ortho}), 8.43 (dd, 3H, $^3J_{H,H}$ = 2.9 Hz, $^3J_{H,P}$ = 0.8 Hz, Pz 5-H). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): 2.51 (N≡C*Me*), 109.7 (d, $^3J_{C,P}$ = 8.9 Hz, Pz C-4), 114.9 (s,

N≡C), 128.4 (s, C_{ortho}), 129.2 (s, C_{meta}), 129.8 (s, C_{ipso}), 131.3 (s, C_{para}), 137.3 (d, $^{2}J_{C,P}$ = 11.6 Hz, Pz C-5), 161.2 (d, $^{3}J_{C,P}$ = 11.9 Hz, Pz C-3). $^{19}F\{^{1}H\}$ NMR (235.4 MHz, CD_2Cl_2): δ −72.9 (d, $^{1}J_{F,P}$ = 711 Hz). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, CD_2Cl_2): δ −144.3 (septet, 1P, $^{1}J_{P,F}$ = 711 Hz, PF_6), −19.8 (s, 1P, PO). IR: ν 3136 (w), 3117 (w), 3059 (w), 1535 (w), 1504 (w), 1454 (w), 1381 (w), 1327 (m), 1300 (m), 1280 (w), 1215 (m), 1161 (m), 1087 (w), 1072 (m), 1030 (s), 952 (m), 756 (s), 690 (s), 609 (s), 586 (s), 505 (m) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{27}H_{21}CuN_6OP$ (M − PF_6 − CH_3CN) 539.0805, found 539.0774.

Copper(I) Acetonitrile Tris(3-*tert*-butylpyrazolyl)phosphine Oxide Hexafluorophosphate (2c). Yield: 85%. Mp: 160–165 °C dec. ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ 1.44 (s, 27H, C*Me*$_3$), 2.34 (s, 3H, N≡C–*Me*), 6.56 (dd, 3H, $^{4}J_{H,P}$ = 4.7 Hz, $^{3}J_{H,H}$ = 3.0 Hz, Pz 4-H), 8.11 (d, 3H, $^{3}J_{H,H}$ = 3.0 Hz, Pz 5-H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 2.9 (s, N≡C–*Me*), 30.0 (s, C*Me*$_3$), 33.1 (s, *C*Me$_3$), 108.0 (d, $^{3}J_{C,P}$ = 8.9 Hz, Pz C-4)), 118.1 (N≡C), 136.2 (d, $^{2}J_{C,P}$ = 11.7 Hz, Pz C-5), 171.7 (d, $^{3}J_{C,P}$ = 10.5 Hz, Pz C-3). $^{19}F\{^{1}H\}$ NMR (235.4 MHz, CD_2Cl_2): δ −73.1 (d, $^{1}J_{F,P}$ = 711 Hz). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, CD_2Cl_2): δ −144.4 (septet, 1P, $^{1}J_{P,F}$ = 711 Hz, PF_6), −20.7 (s, 1P, PO). IR: ν 1531 (w), 1319 (w), 1230 (w), 1188 (w), 1145 (w), 1049 (m), 837 (s), 783 (m), 729 (w), 628 (s), 570 (m), 555 (s), 524 (w), 509 (w), 455 (w), 420 (m). HR ESI-MS: *m*/*z* calcd for $C_{21}H_{33}CuN_6OP$ (M − CH_3CN − PF_6) 479.1744, found 479.1729.

Copper(I) Acetonitrile Tris(3-phenyl-5-methylpyrazolyl)phosphine Oxide Hexafluorophosphate (2d). Yield: 98%. Dec pt: 190–200 °C (no melting). ^{1}H NMR (500.2 MHz, CD_2Cl_2): δ 1.85 (s, 3H, N≡C–*Me*), 2.77 (s, 9H, Pz 5-Me), 6.64 (d, 3H, $^{4}J_{H,P}$ = 4.8 Hz, Pz 4-H), 7.41–7.47 (m, 6H, H_{meta}), 7.47–7.52 (m, 3H, H_{para}), 7.60 (d, 6H, $^{3}J_{H,H}$ = 7.1 Hz, H_{ortho}). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2): 2.3 (s, N≡C–*Me*), 14.0 (s, Pz 5-Me), 110.0 (d, $^{3}J_{C,P}$ = 9.5 Hz, Pz C-4), 116.6 (s, N≡C), 128.2 (s, C_{ortho}), 129.0 (s, C_{meta}), 130.0 (s, C_{ipso}), 130.9 (s, C_{para}), 151.8 (d, $^{2}J_{C,P}$= 11.3 Hz, Pz C-5), 159.5 (d, $^{3}J_{C,P}$ = 11.9 Hz, Pz C-3). $^{19}F\{^{1}H\}$ NMR (235.4 MHz, CD_2Cl_2): δ −73.4 (d, $^{1}J_{F,P}$ = 710 Hz). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, CD_2Cl_2): δ −144.5 (septet, 1P, $^{1}J_{P,F}$ = 710 Hz, PF_6), −18.0 (s, 1P, PO). IR: ν 1566 (w), 1462 (w), 1315 (w), 1292 (w), 1269 (w), 1161 (m), 952 (w), 833 (s), 767 (m), 736 (w), 694 (m), 648 (m), 621 (w), 586 (s), 555 (s) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{32}H_{30}CuN_7OP$ (M − PF_6) 622.1540, found 622.1515.

Copper(I) Acetonitrile Tris(3-*tert*-butyl-5-methylpyrazolyl)phosphine Oxide Hexafluorophosphate (2e). Yield: 96%. Mp: 170–174 °C. ^{1}H NMR (500.2 MHz,

$CDCl_3$): δ 1.35 (s, 27H, CMe_3), 2.34 (s, 3H, N≡C–Me), 2.50 (s, 9H, Pz 5-Me), 6.28 (d, 3H, $^4J_{H,P}$ = 4.7 Hz, Pz 4-H). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): 2.5 (s, N≡C–*Me*), 13.5 (s, Pz 5-Me), 29.9 (s, CMe_3), 32.8 (s, CMe_3), 109.2 (d, $^3J_{C,P}$ = 9.2 Hz, Pz C-4), 118.3 (N≡C), 150.0 (d, $^2J_{C,P}$ = 11.9 Hz, Pz C-5), 169.5 (d, $^3J_{C,P}$ = 10.6 Hz, Pz C-3). $^{19}F\{^1H\}$ NMR (235.4 MHz, $CDCl_3$): δ −73.2 (d, $^1J_{F,P}$ = 712 Hz). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −144.3 (septet, 1P, $^1J_{P,F}$ = 712 Hz, PF_6), −17.1 (s, 1P, PO). IR: ν 2974 (w), 1573 (w), 1284 (w), 1234 (w), 1172 (m), 976 (w), 840 (s), 821 (s), 729 (s), 713 (w), 624 (w), 594 (s), 555 (m), 516 (w) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{24}H_{39}CuN_6OP$ (M − CH_3CN − PF_6) 521.2213, found 521.2197.

Preparation of Copper(I) Triphenylphosphine Tris(3,5-dimethylpyrazolyl)-phosphine Oxide Hexafluorophosphate (3a). Dichloromethane (5 mL) was added with stirring to a mixture of **2a** (87 mg, 0.15 mmol) and triphenylphosphine (41 mg, 0.16 mmol). Within a few minutes a clear solution was obtained, which was stirred for 3 h more. After removal of all volatiles, the residual colorless solid was washed with diethyl ether (3 × 5 mL) and dried *in vacuo* for 5 h at 65 °C, yielding 94 mg (0.12 mmol, 78 %) of **3a**. Crystals, suitable for X-ray structure analysis, were obtained by storing a saturated solution of **3a** in a dichloromethane/pentane mixture at 7 °C for 4 days. Mp: 226.1–226.5 °C. ^1H NMR (250.1 MHz, $CDCl_3$): δ 1.79 (s, 9H, 3-Me), 2.66 (s, 9H, 5-Me), 6.16 (d, 3H, $^4J_{H,P}$ = 5.2 Hz, Pz 4-H), 7.41–7.53 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 13.9 (s, 5-Me), 14.3 (s, 3-Me), 111.5 (d, $^3J_{C,P}$ = 9.9 Hz, Pz C-4), 129.6 (d, $^3J_{C,P}$ = 10.1 Hz, C_{ortho}), 131.3 (d, $^4J_{C,P}$ = 1.8 Hz, C_{para}), 132.0 (d, $^1J_{C,P}$ = 38.5 Hz, C_{ipso}), 134.0 (d, $^2J_{C,P}$ = 15.2 Hz, C_{meta}), 151.0 (d, $^2J_{C,P}$ = 11.7 Hz, Pz C-5), 157.1 (d, $^3J_{C,P}$ = 11.4 Hz, Pz C-3). $^{19}F\{^1H\}$ NMR (235.4 MHz, $CDCl_3$): δ −73.9 (d, $^1J_{F,P}$ = 712 Hz). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −144.4 (septet, 1P, $^1J_{P,F}$ = 712 Hz, PF_6), −20.2 (s, 1P, PO), 6.8 (broad s, 1P, PPh_3). IR: ν 3653 (w), 3113 (w), 3078 (w), 2989 (w), 2935 (w), 2361 (w), 2322 (w), 1574 (m), 1477 (sh), 1462 (w), 1435 (m), 1412 (m), 1373 (w), 1315 (m), 1277 (m), 1177 (m), 1153 (m), 1095 (m), 1034 (w), 976 (w), 833 (vs), 748 (s), 698 (s), 656 (w), 625 (w), 590 (s), 555 (s), 521 (s), 505 (s), 451 (s), 428 (m), 405 (w) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{33}H_{36}CuN_6OP_2$ (M − PF_6) 657.1722, found 657.1647.

General Procedure for MeCN−CO Exchange: A solution of the Cu-acetonitrile complex in degassed dichloromethane (5 mL) was degassed by three freeze−pump−thaw cycles. Before thawing for the third time, the flask was filled

with CO gas (1 atm). After thawing, the reaction mixture was stirred at room temperature for the indicated time. Then, pentane (20 mL) was added and the solvent was removed from the precipitated solid using a cannula filter. Subsequently, the product was dried under a stream of nitrogen.

Copper(I) Carbonyl Tris(3,5-dimethylpyrazolyl)phosphine Oxide Hexafluorophosphate (4a). After stirring for 1 month, a mixture of the **2a** and the product was present in a 0.3 : 1.0 ratio, according to ^{1}H NMR integration. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 2.42 (s, 9H, 3-Me), 2.62 (s, 9H, 5-Me), 6.25 (d, 3H, $^{4}J_{H,P}$ = 4.6 Hz, Pz 4-H). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 13.6 (s, 5-Me), 14.4 (s, 3-Me), 111.2 (d, $^{3}J_{C,P}$ = 9.7 Hz, Pz C-4), 151.4 (d, $^{2}J_{C,P}$ = 10.9 Hz, Pz C-5), 158.4 (d, $^{3}J_{C,P}$ = 10.8 Hz, Pz C-3). ^{19}F{^{1}H} NMR (235.4 MHz, $CDCl_3$): δ −73.5 (d, $^{1}J_{F,P}$ = 712 Hz). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −144.4 (septet, 1P, $^{1}J_{P,F}$ = 712 Hz, PF_6), −21.7 (s, 1P, PO). IR: ν 3148 (w), 3128 (w), 3094 (w), 2129 (w), 1574 (m), 1535 (w), 1451 (w), 1458 (m), 1412 (w), 1377 (w), 1319 (m), 1277 (s), 1173 (s), 1153 (sh), 1099 (w), 1038 (m), 975 (m), 922 (w), 837 (vs), 814 (vs), 764 (s), 725 (m), 694 (m), 625 (m), 582 (vs), 555 (vs), 520 (sh), 451 (s), 420 (sh) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{15}H_{21}CuN_6OP$ (M − PF_6 − CO) 395.0805, found 395.0777.

Copper(I) Carbonyl Tris(3-phenylpyrazolyl)phosphine Oxide Hexafluorophosphate (4b). After stirring overnight, most of **2b** seemed not to have reacted according to NMR spectroscopy. The actual conversion is difficult to estimate from the NMR spectra because of the similarity of the chemical shifts of the product and the starting compound. IR ν(CO): 2121 (w) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{27}H_{21}CuN_6OP$ (M − PF_6 − CO) 539.0805, found 539.0774.

Copper(I) Carbonyl Tris(3-*tert*-butylpyrazolyl)phosphine Oxide Hexafluorophosphate (4c). After stirring for a month, most of the isolated material was unreacted **2c**. According to ^{1}H NMR integration, the ratio of **2c** and the product was 4 : 1. ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 1.36 (s, 27H, C*Me*$_3$), 6.30 (s, 3H, coupling constants are not resolved, Pz 4-H), 7.99 (d, 3H, $^{3}J_{H,H}$ = 2.4 Hz, Pz 5-H). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 30.6 (s, C*Me*$_3$), 32.5 (s, *C*Me$_3$), 107.2 (br s, Pz C-4)), 135.3 (br s, Pz C-5), 166.9 (br s, Pz C-3); coupling constants are not resolved. ^{19}F{^{1}H} NMR (235.4 MHz, $CDCl_3$): δ −73.6 (br d, $^{1}J_{F,P}$ = 715 Hz). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −144.6 (septet, 1P, $^{1}J_{P,F}$ = 711 Hz, PF_6), −19.4 (s, 1P, PO). IR ν(CO): 2118 (w).

Copper(I) Carbonyl Tris(3-phenyl-5-methylpyrazolyl)phosphine Oxide Hexafluorophosphate (4d). Stirring for 64 h gave full conversion and **4d** was isolated as a colorless solid in quantitative yield. Mp: 170–177 °C dec. ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 2.81 (s, 9H, Pz 5-Me), 6.64 (d, 3H, $^{4}J_{H,P}$ = 5.0 Hz, Pz 4-H), 7.44–7.62 (m, 15H, Ph). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ 14.1 (s, Pz *5-Me*), 110.6 (br s, Pz C-4), 128.3 (s, C_{ortho}), 129.5 (s, C_{meta}), 130.1 (s, C_{ipso}), 131.1 (s, C_{para}), 152.9 (br s, Pz C-3), 161.1 (br s, Pz C-5). ^{19}F{^{1}H} NMR (235.4 MHz, CD_2Cl_2): δ −73.2 (d, $^{1}J_{F,P}$ = 711 Hz). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ −144.4 (septet, 1P, $^{1}J_{P,F}$ = 711 Hz, PF_6), −20.4 (s, 1P, PO). IR: ν 2111 (w), 1565 (w), 1458 (w), 1407 (w), 1332 (w), 1271 (w), 1162 (m), 958 (w), 832 (s), 771 (m), 703 (m), 699 (m), 584 (s), 555 (s) cm^{-1}. HR ESI-MS: *m*/*z* calcd for $C_{30}H_{27}CuN_6OP$ (M − PF_6 − CO) 581.1274, found 581.1241.

Crystal Structure Determinations. X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) (compounds **2c,d**) or on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) (compound **3a**). Integration was performed with Saint[45] (**2c,d**) or Eval15[46] (**3a**). The structures were solved with direct methods using SHELXS-97.[47] Least squares refinement was performed with SHELXL-97[47] on F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions (**2c, 3a**) or located in difference Fourier maps (**2d**) and refined with a riding model. Structure calculations and checking for higher symmetry were performed with PLATON.[48] Further details are given in Table 2.3. For **2c,d**, distance and angle restraints were used for the PF_6 anions. The F atoms were restrained to approximate isotropic behavior. For **3a**, the crystal appeared to be cracked into two fragments related by a rotation of 1.5° about an arbitrary axis. The integration was performed with two orientation matrices to generate an HKLF5 file.[49] Distance and angle restraints were used for the CH_2Cl_2 solvent molecules. The Cl atoms were restrained to approximate isotropic behavior.

Table 2.3. Experimental Details of the Crystal Structure Determinations.

	2c	**2d**	**3a**
formula	$[C_{23}H_{36}CuN_7OP](PF_6)$ $\cdot CH_2Cl_2$	$[C_{32}H_{30}CuN_7OP](PF_6)$	$[C_{33}H_{36}CuN_6OP_2](PF_6)$ $\cdot 2CH_2Cl_2$
fw	750.99	768.11	972.98
crystal size [mm³]	0.60x0.51x0.31	0.42x0.25x0.21	0.51x0.28x0.18
crystal color	Colorless	Colorless	colorless
T [K]	150(2)	150(2)	150(2)
crystal system	Orthorhombic	Monoclinic	triclinic
space group	$P2_12_12$ (no. 18)	$P2_1/c$ (no. 14)	$P\overline{1}$ (no. 2)
a [Å]	16.9778(6)	8.6120(3)	11.0739(3)
b [Å]	18.8108(7)	23.4829(9)	12.6624(3)
c [Å]	10.5559(4)	17.3556(6)	15.9619(2)
α [°]	-	-	102.223(1)
β [°]	-	109.357(2)	106.463(1)
γ [°]	-	-	91.278(1)
V [Å³]	3371.2(2)	3311.5(2)	2089.69(8)
Z	4	4	2
d_{calc} [g/cm³]	1.480	1.541	1.546
μ [mm⁻¹]	0.965	0.829	0.958
abs. corr. type	multi-scan[50]	multi-scan[50]	multi-scan[50]
abs. corr. range	0.67–0.75	0.68–0.75	0.70–0.84
$(\sin\theta/\lambda)_{max}$ [Å⁻¹]	0.65	0.65	0.65
refl. Measured / unique	46498 / 7748	57072 / 7613	40560 / 9572
parameters / restraints	401 / 91	468 / 81	531 / 42
R1/wR2 [I>2σ(I)]	0.0326 / 0.0925	0.0294 / 0.0761	0.0349 / 0.0887
R1/wR2 [all refl.]	0.0337 / 0.0936	0.0337 / 0.0795	0.0409 / 0.0937
S	1.023	1.032	1.032
Flack x[51]	−0.009(10)	-	-
$\rho_{min/max}$ [e/Å³]	−0.48 / 0.69	−0.41 / 0.63	−0.72 / 0.87

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