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Phospha-Scorpionate Complexes by Click Chemistry using Phenyl Azide and Ethynylphosphine Oxides

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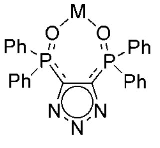
The copper-catalyzed Click reaction of phenyl azide with ethynylphosphine oxides provides new P-substituted triazoles. With tris(ethynyl)phosphine oxide this route affords a versatile scorpionate ligand that coordinates to $RhCl_3$ as a tripodal N ligand. Upon reduction, the same ligand can act as a P donor to $W(CO)_5$. Both coordination modes can be combined, giving access to a bimetallic Mo/W complex.

Introduction

Scorpionates are tripodal N ligands ubiquitous in both coordination chemistry and homogeneous catalysis.[1] In these ligands two pyrazolyl groups form a chelate, while the third (pyrazolyl) donor may act like a "scorpion tail" grabbing its prey as it complexes the common metal. Their functionality was extended only recently with hetero substituents[2] on the pyrazole rings to enable coordination on the apex face of the molecular frame. Commonly the apex of scorpionates consists of anionic borates[1] or neutral hydrocarbons.[3] Here we report on (bi)metallic complexes of novel scorpionates having a phosphorus apex and triazoles as N ligands.

Triazoles are readily obtained by a Huisgen 1,3-dipolar cycloaddition[4] of organic azides to alkynes. The Cu^I-catalyzed version of this click reaction[5] tolerates many functional groups (e.g., esters, acids, alkenes, alcohols, and amines) and yields only the 1,4-disubstituted derivatives,[6] which are exploited heavily in a diversity of fields.[7–9] Phospha-substituted triazoles are rare[10] but add an extra dimension, as in the O,O- and N,O-chelating **1a**,**b**.[11] Also illustrative is ClickPhos (**2**), which is an effective ligand in Pd-catalyzed Suzuki–Miyaura coupling[12,13] and is synthesized by "P-substitution" of the triazole ring.



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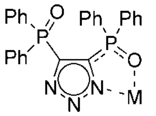

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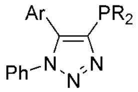

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Results and Discussion

Phospha-substituted 1,2,3-triazoles can be obtained directly by the stereoselective cycloaddition of azides to P-substituted alkynes, but protection of the phosphorus center is necessary

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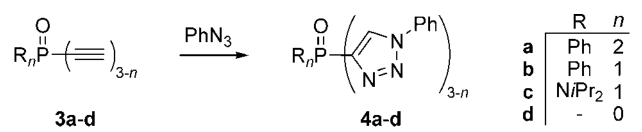
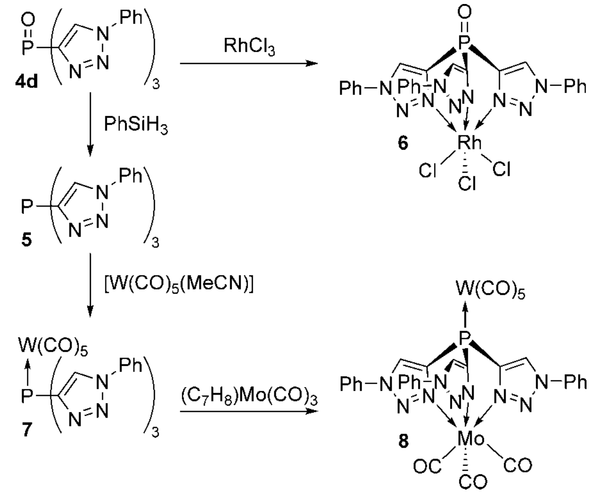
Scheme 1. Syntheses of P-Substituted 1,2,3-Triazoles 4



Scheme 2. Syntheses of Complexed Phospha-Scorpionates 6−8



to prevent the Staudinger reaction to occur.[13,14] The thus required phosphinoyl-ethynes **3a−d**, having one to three terminal acetylenic groups, were synthesized by reacting $R_nP(=O)X_{3-n}$ (R = Ph, N*i*Pr$_2$; X = Cl, Br; *n* = 0−2) with $Me_3SiC\equiv CMgBr$, followed by desilylation using *n*Bu$_4$NF. Subsequent addition of phenyl azide under click conditions ($CuSO_4\cdot 5H_2O$, sodium ascorbate, H_2O/*t*BuOH)[5b] results exclusively in the 1,4-disubstituted 1,2,3-triazoles **4a−d**, which are easily obtained in pure form after column chromatography (>70% yield; Scheme 1).

An interesting application is the reduction of **4a** (R = Ph, *n* = 2; $\delta(^{31}P)$ 17.4) in $PhSiH_3$ at 100 °C (12 h) to give the novel ClickPhos ligand[12] **2a** (R = Ph, no Ar; $\delta(^{31}P)$ −32.4) as a colorless solid in 94% isolated yield. Phospha-scorpionate **4d** ($\delta(^{31}P)$ −5.7), obtained in 72% yield from tris(ethynyl)phosphine oxide **3d** ($\delta(^{31}P)$ −56.8) by a triple click reaction, is also amenable to reduction with $PhSiH_3$ at 100 °C (48 h), affording the corresponding phosphine **5** as an air-sensitive, off-white solid (90% yield; $\delta(^{31}P)$ −83.7).

Both novel scorpionates, **4d** and **5**, are susceptible to transition-metal complexation, but in different manners. Phosphine oxide **4d** functions as a tripodal N ligand and coordinates to rhodium trichloride in refluxing THF/EtOH to give the novel **6** as an orange solid (65% yield; Scheme 2), thereby behaving like the related tris(pyrazolyl)phosphine oxides[15] that complex to Cu^I,[15b] $ZnCl_2$,[15b] Tl^I,[15c] and $Mo(CO)_3$.[15d] The Rh phospha-scorpionate complex **6** shows a ^{31}P NMR signal at −9.7 ppm and a deshielded ^1H NMR signal at 10.00 ppm (cf. **4d**, 8.87 ppm) for the three triazole ring protons. A single-crystal X-ray structural analysis confirmed the coordination of $RhCl_3$ to the 3-position of the three triazole rings (Figure 1). The molecular structure is propeller-shaped, with the three phenyl groups rotated by 37.9(3), 16.2(3), and 17.7(3)° in the same direction from the planar triazole rings. The P═O group and the Rh transition metal are on the axle of the propeller (O1−P1−Rh1 = 179.42(14)°), and the angles around Rh (88.17(15)−92.55(4)°) are close to the ideal 90° for an octahedron.

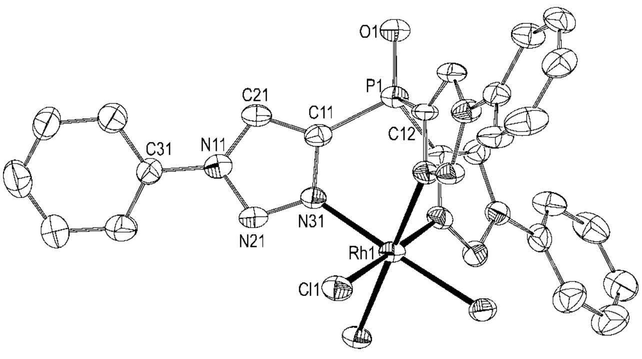


Figure 1. Displacement ellipsoid plot of **6** drawn at the 50% probability level. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1−Cl1 = 2.3187(12), Rh1−N31 = 2.057(4), P1−O1 = 1.463(3), P1−C11 = 1.781(5), N11−N21 = 1.352(5), N21−N31 = 1.308(5), N11−C21 = 1.354(6), N11−C31 = 1.435(6), N31−C11 = 1.369(6), C11−C21 = 1.364(6); O1−P1−Rh1 = 179.42(14), O1−P1−C11 = 116.8(2), C11−P1−C12 = 99.9(2), Rh1−N31−N21 = 125.1(3), N31−C11−C21 = 106.0(4).

Reaction of phosphine **5** with $[W(CO)_5(MeCN)]$ in THF (room temperature, 16 h) gave the stable W complex **7** (86% yield, mp 211−212 °C; Scheme 2) with the transition-metal group connected to the phosphorus atom instead of to the triazole rings, as evidenced by the $^1J(P,W)$ coupling constant of 257.2 Hz for the ^{31}P NMR signal at −40.6 ppm. The structure of **7** was established unequivocally by a single-crystal X-ray analysis (Figure 2), which shows an octahedral arrangement for the W metal center surrounded by five CO ligands and the apex P of ligand **5** (W1−P1 = 2.4829(10) Å). The P−C bond lengths are in the expected range, and the nitrogens of the triazole rings are mostly facing outward.

Bimetallic complexation of scorpionate **5** can also be realized. Reaction of **7** with $[(C_7H_8)Mo(CO)_3]$ in THF (room temperature, 16 h) results in the desired W/Mo-bimetallic complex **8** as a red solid (74% yield; $\delta(^{31}P)$ −62.8, $^1J(P,W)$ = 261.1 Hz; Scheme 2). $Mo(CO)_3$ complexation to **7** causes an upfield shift of 22.2 ppm for the ^{31}P NMR signal and of 4.5 ppm for the axial carbonyl signal of the $W(CO)_5$ group ($\delta(^{13}C)$ 194.6, $^2J(C,P)$ = 25.5 Hz); the ^1H NMR signal of the triazole hydrogen is not influenced ($\delta(^1H)$ 8.59 for **8** vs 8.53 for **7**). The X-ray structure of **8** (Figure 3) shows the binding of the $Mo(CO)_3$ unit to the 3-position of the three triazoles analogous to Rh complex **6**. This coordination elongates the (cage) C−N bonds (C1−N3: **8**, 1.374(4)−1.384(4) Å; **7**, 1.351(4)−1.371(4) Å) and slightly reduces the sum of the angles around P (**8**, 298.91°; **7**, 303.34°) that contributes to the shielding of the ^{31}P NMR signal.[16] A near-octahedral arrangement is observed for both metals, with the Mo-centered one being the most distorted: i.e., the average N−Mo−N, C−Mo−C, and N−Mo−C angles are 81.2, 86.5, and 96.1°, respectively.

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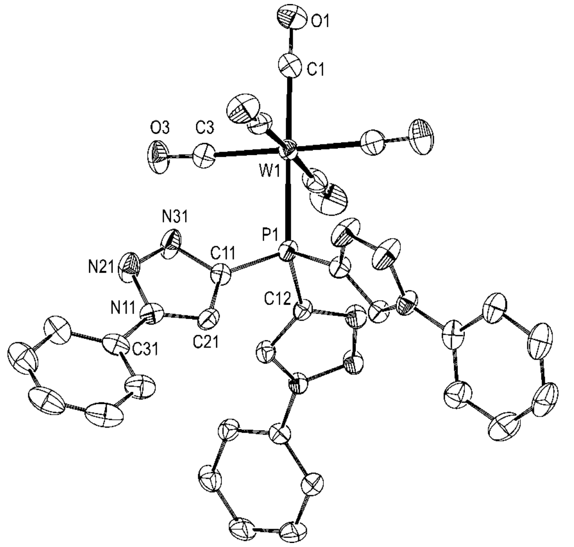

Figure 2. Displacement ellipsoid plot of **7** drawn at the 50% probability level. Hydrogen atoms and cocrystallized THF are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−P1 = 2.4829(10), W1−C1 = 2.003(4), W1−C3 = 2.059(4), P1−C11 = 1.810(4), C1−O1 = 1.147(5), C3−O3 = 1.138(4), C11−C21 = 1.372(5), C11−N31 = 1.351(4), C21−N11 = 1.338(5), N11−N21 = 1.342(4), N21−N31 = 1.304(4), C31−N11 = 1.442(5); P1−W1−C1 = 174.79(12), W1−P1−C11 = 115.80(12), C11−P1−C12 = 101.74(16).

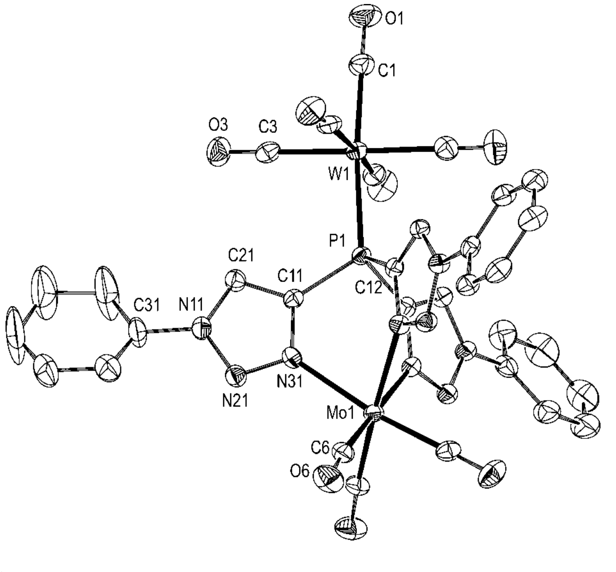

Figure 3. Displacement ellipsoid plot of **8** drawn at the 50% probability level. Hydrogen atoms and cocrystallized THF are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−P1 = 2.4760(8), W1−C1 = 2.012(3), W1−C3 = 2.049(3), Mo1−C6 = 1.951(4), Mo1−N31 = 2.277(3), P1−C11 = 1.810(3), C1−O1 = 1.149(4), C3−O3 = 1.134(4), C6−O6 = 1.168(4), C11−C21 = 1.368(4), C11−N31 = 1.376(4), C21−N11 = 1.340(4), N11−N21 = 1.362(4), N21−N31 = 1.319(4), C31−N11 = 1.434(4); P1−W1−C1 = 173.90(10), W1−P1−C11 = 120.48(10), C11−P1−C12 = 98.91(14), N11−C21−C11 = 105.5(3), N21−N11−C21 = 111.5(3), N11−N21−N31 = 105.8(2), N21−N31−C11 = 109.8(2).

Conclusions

In summary, a new phospha-based scorpionate has been designed with three 1,2,3-triazole rings that is conveniently synthesized by the click reaction between phenyl azide and tris(ethynyl)phosphine oxide. Transition-metal coordination occurs to the phosphorus apex face, to the three triazole rings, and even to both sites when two metals are used. The present results demonstrate a simple and effective molecular design to novel scorpionates with ample opportunities for expansion and application.[17] Homogenous catalysis is an obvious area to explore their potential, but also the communication between the metallic centers is an intriguing facet for further study.

Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. Phenyl azide,[18] tricarbonyl(cycloheptatriene)molybdenum,[19] W(CO)$_5$(acetonitrile),[20] and **3c**[21c] have been prepared according to literature procedures. NMR spectra were recorded at 298 K on a Bruker Avance 250 or on a Bruker Avance 400 spectrometer (^{1}H, ^{13}C, and ^{31}P; 85% H_3PO_4) and referenced internally to residual solvent resonances (^{1}H 7.26 ppm and ^{13}C{^{1}H} 77.16 ppm for CHCl$_3$; ^{1}H 5.32 ppm and ^{13}C{^{1}H} 53.8 ppm for CDHCl$_2$; ^{1}H 7.16 ppm and ^{13}C{^{1}H} 128.06 ppm for C$_6$D$_5$H; ^{1}H 2.49 ppm and ^{13}C{^{1}H} 39.5 ppm for DMSO-*d*$_6$). High-resolution mass spectra (HR EI-MS) were recorded on a Finnigan Mat 900 (70 eV) and fast atom bombardment (HR FAB-MS) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program; samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with Xenon atoms with an energy of 3 keV. During the HR FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used. IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich, Switzerland.

(Diphenylphosphinoyl)acetylene (3a).[21a] Me$_3$SiC≡CMgBr (0.5 M in THF; 70 mL, 35 mmol) was added slowly at 0 °C to a solution of Ph$_2$P(O)Cl (8.28 g, 35 mmol) in THF (50 mL). The reaction mixture was stirred for 0.5 h at 0 °C and subsequently for 1 h at room temperature. Evaporation of the solvent and filtration over silica gel with ethyl acetate as eluent gave pure Ph$_2$P(O)C≡CSiMe$_3$[21a] (9.55 g, 91%) as a light brown solid. Removal of the silyl group was established by dissolving Ph$_2$P(O)C≡CSiMe$_3$ in THF (150 mL), H_2O (0.5 mL) was added, and the reaction mixture was cooled to −78 °C. TBAF on silica (500 mg, 1−1.5 mmol of fluoride/g) was added, the reaction mixture was then slowly warmed to room temperature, and additional H_2O (1 mL) was added. Volatiles were evaporated and the crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) as eluent, affording **3a**[21a] as a colorless solid (6.50 g, 81%). Mp: 55−56 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 3.32 (d, ^3J(H,P) = 9.7 Hz, 1H; ≡C*H*), 7.46−7.54 (m, 6H; Ph*H*), 7.80−7.89 (m, 4H; Ph); ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 79.0 (d, ^1J(C,P) = 160.2 Hz; P*C*≡), 95.8 (d, ^2J(C,P) = 27.7 Hz; ≡*C*H), 128.9 (d, ^3J(C,P) = 13.6 Hz; *m*-Ph), 131.1 (d, ^2J(C,P) = 11.3 Hz; *o*-Ph),

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132.4 (d, ^1J(C,P) = 122.0 Hz; *ipso*-Ph), 132.8 (d, ^4J(C,P) = 3.0 Hz; *p*-Ph). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ 9.5 (s). HR EI-MS: calcd for $C_{14}H_{11}OP$ 226.0548, found 226.0541; *m/z* (%) 226 (100) [M]$^+$.

(Diethynylphosphinoyl)benzene (3b).[21b] $Me_3SiC\equiv CMgBr$ (~0.4 M in THF; 30 mmol) was added dropwise at 0 °C to a solution of PhP(O)Cl$_2$ (2.61 g, 15 mmol) in THF (50 mL); subsequently the reaction mixture was slowly warmed to room temperature, after which ^{31}P NMR showed complete conversion to the product. After evaporation of the solvent, the remaining dark brown oil was dissolved in diethyl ether (400 mL) and extracted with H_2O (2 × 200 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was then dissolved in THF (50 mL) and 0.5 mL of H_2O was added, after which TBAF on silica (500 mg, 1−1.5 mol % of fluoride/g) was added at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for another 1 h. Volatiles were evaporated, and the crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) as eluent, affording **3b**[21b] as a brownish solid (1.42 g, 54%). Mp: 83−84 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 3.40 (d, ^3J(H,P) = 11.0 Hz, 2H; ≡C*H*), 7.45−7.52 (m, 3H; Ph*H*), 7.82−7.92 (m, 2H; Ph*H*). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 78.7 (d, ^1J(C,P) = 194.2 Hz; P*C*≡), 93.9 (d, ^2J(C,P) = 35.9 Hz; ≡*C*H), 129.4 (d, ^3J(C,P) = 15.3 Hz; *m*-Ph), 130.8 (d, ^2J(C,P) = 12.8 Hz; *o*-Ph), 131.4 (d, ^1J(C,P) = 142.6 Hz; *ipso*-Ph), 133.8 (d, ^4J(C,P) = 3.1 Hz; *p*-Ph). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ −19.5 (s). IR (CH$_2$Cl$_2$): ν 3287 (m, C−H), 2061 (s, C≡C), 1207 cm^{-1} (s; P=O). HR EI-MS: calcd for $C_{10}H_7OP$ 174.0234, found 174.0225; *m/z* (%) 174 (100) [M]$^+$.

(Diisopropylamino)diethynylphosphine Oxide (3c).[21c] $Me_3SiC\equiv CMgBr$ (2 equiv, ~0.4 M in THF) was added dropwise at 0 °C to a solution of ^{i}Pr$_2$NP(O)Br$_2$ (950 mg, 3.1 mmol) in THF (10 mL), and the reaction mixture was slowly warmed to room temperature; the ^{31}P NMR spectrum showed complete conversion to the product. The light brown residual oil, obtained after solvent evaporation, was dissolved in diethyl ether (400 mL), washed with H_2O, and dried over $MgSO_4$. The crude product was dissolved in wet THF (50 mL), and TBAF on silica (250 mg, 1−1.5 mol % of fluoride/g) was added at 0 °C. The reaction mixture was stirred for 1 h and quenched with H_2O. Volatiles were evaporated, and the crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) as eluent, affording **3c**[21c] as a light yellow solid (415 mg, 68%). Mp: 134−135 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 1.31 (d, ^3J(H,H) = 6.8 Hz, 12H; C*H*$_3$), 3.05 (d, ^3J(H,P) = 11.6 Hz, 2H; ‘C*H*), 3.60−3.74 (m, ^3J(H,P) = 21.2 Hz, ^3J(H,H) = 6.8 Hz, 2H; NC*H*). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 22.5 (d, ^3J(C,P) = 2.1 Hz; *C*H$_3$), 46.9 (d, ^2J(C,P) = 6.9 Hz; N*C*H), 81.1 (d, ^1J(C,P) = 224.7 Hz; P*C*≡), 88.3 (d, ^2J(C,P) = 41.5 Hz; ≡*C*H). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ −21.4 (s). IR (CH$_2$Cl$_2$): ν 3285 (m, C−H), 2063 (m, C≡C), 1238 cm^{-1} (m, P=O);. HR EI-MS: calcd for $C_{10}H_{16}NOP$ 197.0970, found 197.0969; *m/z* (%) 197 (8) [M]$^+$.

Tris(ethynyl)phosphine Oxide(3d).[21d] A freshly prepared solution of $Me_3SiC\equiv CMgBr$ (~0.3 M in THF) was added dropwise at 0 °C to a solution of P(O)Cl$_3$ (307 mg, 2.00 mmol) in THF (10 mL) until ^{31}P NMR showed complete conversion of the starting material. The remaining acetylenic Grignard reagent was quenched with H_2O. The dark brown reaction mixture was warmed to room temperature, and the solvent was evaporated under reduced pressure. H_2O (50 mL) was added, and extraction with diethyl ether (2 × 50 mL) gave a dark brown oil, which was purified by filtration over silica gel with ethyl acetate as eluent. The ^{31}P NMR spectrum showed the formation of several triethynylphosphine oxides resulting from partial desilylation. Dissolving the dark brown oil in THF/H_2O (20 mL/0.25 mL) with TBAF on silica (250 mg, 1−1.5 mol % of fluoride/g) and stirring the solution for 1 h resulted in complete desilylation. Volatiles were evaporated, and the crude product was purified by column chromatography over silica gel with ethyl acetate as eluent, affording **3d**[21d] (133 mg, 55%) as a pale white solid, which was stored at −30 °C to avoid decomposition. Mp: 111−112 °C. ^{1}H NMR (250.1 MHz, C$_6$D$_6$): δ 2.15 (d, ^3J(H,P) = 12.3 Hz; ≡C*H*). ^{13}C{^{1}H} NMR (62.9 MHz, C$_6$D$_6$): δ 78.8 (d, ^1J(C,P) = 228.5 Hz; P*C*≡), 91.8 (d, ^2J(C,P) = 44.2 Hz; ≡*C*H). ^{31}P{^{1}H} NMR (101.3 MHz, C$_6$D$_6$): δ −56.8 (s). IR (CH$_2$Cl$_2$): ν 3280 (m, C−H), 2068 (s, C≡C), 1235 cm^{-1} (m, P=O). HR EI-MS: calcd for C_6H_3OP 121.9922, found 121.9916; *m/z* (%) 122 (6) [M]$^+$.

4-(Diphenylphosphinoyl)-1-phenyl-1*H*-1,2,3-triazole (4a). Sodium ascorbate (0.10 mmol, 100 μL of a freshly prepared 1 M solution in H_2O), followed by $Cu^{II}SO_4\cdot 5H_2O$ (3.0 mg, 0.01 mmol), dissolved in H_2O (50 μL), were added to a suspension of **3a** (226 mg, 1.00 mmol) and phenyl azide (119 mg, 1.00 mmol) in a 1:1 mixture of H_2O and ^{t}BuOH (4 mL). The reaction mixture was stirred for 16 h, during which time a light yellow solid precipitated. The reaction mixture was extracted with DCM (2 × 10 mL) and dried over $MgSO_4$, volatiles were evaporated, and the crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) as eluent, followed by 1% ethanol in ethyl acetate, affording **4a** as a colorless solid (248 mg, 72%). Mp: 191−192 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 7.49−7.55 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.74 (d, ^3J(H,H) = 7.1 Hz, 2H; *o*-Ph*H*-N), 7.90−7.99 (m, 4H; *o*-Ph*H*-P), 8.63 (s, 1H; =C*H*). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 121.0 (s; *o*-Ph-N), 128.8 (d; ^3J(C,P) = 12.8 Hz; *m*-Ph-P), 129.6 (s; *p*-Ph-N), 130.2 (s; *m*-Ph-N), 131.8 (d; ^2J(C,P) = 9.7 Hz; *o*-Ph-P), 132.5 (s; *p*-Ph-P), 129.3 (d; ^2J(C,P) = 23.5 Hz; PC=*C*H), 132.5 (d, ^1J(C,P) = 110.5 Hz; *ipso*-Ph-P), 136.7 (s; *ipso*-Ph-N), 143.1 (d, ^1J(C,P) = 143.2 Hz; P*C*=CH). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ 17.4 (s). HR FAB-MS: calcd for $C_{20}H_{17}N_3OP$ (*M* + H) 346.1109, found 346.1110; *m/z* (%) 346 (100) [M]$^+$.

4-(Diphenylphosphanyl)-1-phenyl-1*H*-1,2,3-triazole (2a). A mixture of **4a** (345 mg, 1.00 mmol) and PhSiH$_3$ (875 mg, 8.1 mmol) was heated at 100 °C for 12 h. After evaporation of excess PhSiH$_3$, the remaining white solid was dissolved in diethyl ether and filtered over a short path of silica gel. Solvents were evaporated, and the residue was extracted into hexane, affording, after evaporation of all volatiles, **2a** as a colorless solid (310 mg, 94%). Mp: 119−120 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 7.34−7.68 (m, 13H; Ph*H*), 7.68 (m, 2H; *o*-Ph*H*-N), 7.81 (s, 1H; =C*H*). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 120.9 (s; *o*-Ph-N), 127.5 (d, ^2J(C,P) = 24.0 Hz; PC=*C*H), 128.8 (d, ^3J(C,P) = 7.3 Hz; *m*-Ph-P), 129.0 (s; *p*-Ph-N), 129.4 (s; *m*-Ph-N), 130.0 (s; *p*-Ph-P), 133.9 (d, ^2J(C,P) = 20.0 Hz; *o*-Ph-P), 136.3 (d, ^1J(C,P) = 6.6 Hz; *ipso*-Ph-P), 137.1 (s; *ipso*-Ph-N), 145.9 (d, ^1J(C,P) = 6.7 Hz; P*C*=CH). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ −32.4 (s). HR FAB-MS: calcd for $C_{20}H_{17}N_3P$ (*M* + H) 330.1160, found 330.1163; *m/z* (%) 330 (100) [M]$^+$.

(Bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphinoyl)benzene (4b). Sodium ascorbate (0.3 mmol, 0.3 mL of a freshly prepared 1 M solution in H_2O), followed by $Cu^{II}SO_4\cdot 5H_2O$ (15 mg, 0.06 mmol), dissolved in H_2O (100 μL), were added to a suspension of **3b** (509 mg, 2.93 mmol) and phenyl azide (700 mg, 5.88 mmol) in a 1:1 mixture of H_2O and ^{t}BuOH (12 mL). The reaction mixture was stirred for 16 h, during which time a light yellow solid precipitated. The reaction mixture was extracted with DCM and dried over $MgSO_4$, volatiles were evaporated, and the crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (1:1) as eluent, followed by 1% ethanol in ethyl acetate, affording **4b** as a colorless solid (890 mg, 74%). Mp: 179−180 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 7.43−7.56 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.73 (d, ^3J(H,H) = 7.1 Hz, 4H; *o*-Ph*H*-N), 8.10−8.19 (m, 2H; o-Ph*H*-P), 8.57 (s, 2H; =C*H*). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 121.2 (s; *o*-Ph-N), 129.0 (d, ^2J(C,P) = 26.5 Hz; PC=*C*H), 129.0 (d, ^3J(C,P) = 13.4 Hz; *m*-Ph-P), 129.8 (s; *p*-Ph-N), 130.2 (s; *m*-Ph-N), 131.8 (d, ^2J(C,P) = 10.6 Hz; *o*-Ph-P), 133.1 (s; *p*-Ph-P), 136.6 (s; *ipso*-Ph-N), 142.7 (d, ^1J(C,P) = 144.8 Hz;

P*C*═CH), *ipso*-Ph-P could not be resolved. $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ 5.3 (s). HR FAB-MS: calcd for $C_{22}H_{18}N_6OP$ (M + H) 413.1280, found 413.1280; *m/z* (%) 413 (100) $[M]^+$.

Bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)(diisopropylamino)phosphine Oxide (4c). Sodium ascorbate (0.60 mmol, 600 μL of a freshly prepared 1 M solution in H_2O), followed by $Cu^{II}SO_4 \cdot 5H_2O$ (15.0 mg, 0.06 mmol), dissolved in H_2O (100 μL), were added to a suspension of **3c** (600 mg, 3.07 mmol) and phenyl azide (730 mg, 6.14 mmol) in a 1:1 mixture of H_2O and ^{t}BuOH (12 mL). The reaction mixture was stirred for 16 h, during which time a light brown solid precipitated. After filtration, volatiles were evaporated and the crude product was purified by column chromatography over silica gel with ethyl acetate/ethanol (95:5) as eluent, affording **4c** as a light yellow solid (0.97 g, 72%). Mp: 231−232 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 1.34 (d, ^{3}J(H,H) = 6.7 Hz, 12H; $CH(CH_3)_2$), 3.69−3.82 (m, 2H; $CH(CH_3)_2$), 7.43−7.57 (m, 6H; *m*-Ph*H*, *p*-Ph*H*), 7.75−7.80 (m, 4H; *o*-Ph*H*), 8.48 (s, 2H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ 23.1 (d, ^{3}J(C,P) = 1.8 Hz; $CH(CH_3)_2$), 47.0 (d, ^{2}J(C,P) = 5.9 Hz; $CH(CH_3)_2$), 121.0 (s; *o*-Ph), 128.3 (d, ^{2}J(C,P) = 28.6 Hz; PC═*C*H), 129.5 (s; *p*-Ph), 130.2 (s; *m*-Ph), 136.8 (s; *ipso*-Ph), 144.9 (d, ^{1}J(C,P) = 167.9 Hz; P*C*═CH). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ 7.8 (s). HR FAB-MS: calcd for $C_{22}H_{27}N_7OP$ (M + H) 436.2015, found 436.2027; *m/z* (%) 436 (100) $[M]^+$.

Tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine Oxide (4d). Sodium ascorbate (0.2 mmol, 200 μL of a freshly prepared 1 M solution in H_2O), followed by $Cu^{II}SO_4 \cdot 5H_2O$ (8 mg, 0.03 mmol), dissolved in H_2O (50 μL), were added to a suspension of **3d** (139 mg, 1.14 mmol) and phenyl azide (417 mg, 3.51 mmol) in a 1:1 mixture of H_2O and ^{t}BuOH (4 mL). The reaction mixture was stirred for 18 h, during which time a brown solid precipitated. Fifteen milliliters of H_2O and 2 mL of saturated aqueous NH_4Cl were added, and the mixture was extracted with DCM (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, and all solids were removed by filtration over Celite. The Celite plug was washed with DCM (3 × 8 mL), and all volatiles were thoroughly evaporated from the clear yellow filtrates. To remove residual ^{t}BuOH, the resulting pale foam was redissolved in 12 mL of DCM and again taken to dryness, affording **4d** as a light yellow solid still containing 0.39 equiv of DCM (465 mg, 80%). **4d**·0.5DCM can be obtained as pale crystals from DCM/pentane at −20 °C. Mp: 201−202 °C. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 5.29 (s; DCM), 7.48−7.58 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.77 (d, ^{3}J(H,H) = 6.9 Hz, 6H; *o*-Ph*H*), 8.87 (s, 3H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ 53.5 (s, DCM), 121.1 (s; *o*-Ph), 129.6 (s; *p*-Ph), 129.6 (d, ^{2}J(C,P) = 28.6 Hz; PC═*C*H), 130.0 (s; *m*-Ph), 136.4 (s; *ipso*-Ph), 141.0 (d, ^{1}J(C,P) = 157.1 Hz; P*C*═CH). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ −5.7 (s). HR FAB-MS: calcd for $C_{24}H_{19}N_9OP$ (M + H) 480.1450, found 480.1447; *m/z* (%) 480 (100) $[M]^+$. Anal. Calcd for $C_{24.5}H_{19}ClN_9OP$ (**4d** + 0.5 equiv of DCM): C, 56.38; H, 3.67; N, 24.15. Found: C, 56.44; H, 3.82; N, 24.26.

Tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphane (5). A mixture of **4d** (500 mg, 1.04 mmol) and $PhSiH_3$ (875 mg, 8.1 mmol) was heated at 100 °C for 48 h. After evaporation of excess $PhSiH_3$, the remaining white solid was washed with hexanes, affording, after drying in vacuo, **5** as an air-sensitive off-white solid (430 mg, 90%). Mp: 197−198 °C dec. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.43−7.54 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.72−7.76 (m, 6H; *o*-Ph*H*), 8.42 (s, 3H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ 121.0 (s; *o*-Ph), 128.1 (d, ^{2}J(C,P) = 23.5 Hz; PC═*C*H), 129.3 (s; *p*-Ph), 130.1 (s; *m*-Ph), 137.0 (s; *ipso*-Ph), 142.7 (d, ^{1}J(C,P) = 4.5 Hz; P*C*═CH). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ −83.7 (s). HR-FAB-MS: calcd for $C_{24}H_{19}N_9P$ (M + H) 464.1501, found 464.1507; *m/z* (%) 464 (72) $[M]^+$.

(κ^3-OP(C_2HN_3Ph)$_3$)$RhCl_3$ (6). $RhCl_3 \cdot xH_2O$ (135 mg, 0.6 mmol) was added to a solution of **4d** (280 mg, 0.58 mmol) in THF/EtOH (1 mL/20 mL), and the reaction mixture was stirred under reflux for 3 h. An orange solid precipitated immediately, which was filtered off and dried in vacuo to afford **6** (0.26 g, 65%). Orange needles, suitable crystals for X-ray crystallography, were obtained by slowly diffusing ethanol into a saturated solution of **6** in DMSO. Mp: 271−272 °C dec. ^{1}H NMR (250.1 MHz, DMSO-d_6): δ 7.56−7.71 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.90 (m, 6H; *o*-Ph*H*), 10.00 (s, 3H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, DMSO-d_6): δ 121.4 (s; *o*-Ph), 130.1 (s; *m*-Ph), 130.6 (s; *p*-Ph) 131.1 (s; PC═*C*H), 135.4 (d, ^{1}J(C,P) = 149.8 Hz; P*C*═CH), 135.5 (s; *ipso*-Ph). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, DMSO-d_6): δ −9.7 (s). HR FAB-MS: $C_{24}H_{19}N_9Cl_3OPRh$ (M + H) calcd 687.9571, found 687.9565; *m/z* (%) 688 (5) $[M]^+$, 652 (46) $[M - H - Cl]^+$.

(PhN_3C_2H)$_3$PW(CO)$_5$ (7). **5** (690 mg, 1.49 mmol) was added to a solution of freshly prepared $W(CO)_5(MeCN)$[20] (700 mg, 1.91 mmol) in dry THF (30 mL), and the yellow solution was stirred for 16 h at room temperature. The volatiles were evaporated, and the remaining dark yellow foam was purified by column chromatography over silica gel with DCM as eluent, followed by ethyl acetate/hexane (1:1), affording **7** as a light yellow crystalline solid (1.01 g, 86%). Suitable crystals for X-ray crystallography were obtained from THF/hexane at −20 °C. Mp: 211−212 °C dec. ^{1}H NMR (250.1 MHz, $CDCl_3$): δ 7.43−7.56 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.73−7.77 (m, 6H; *o*-Ph*H*), 8.55 (s, 3H; ═C*H*). ^{1}H NMR (250.1 MHz, CD_2Cl_2): δ 7.44−7.64 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.71−7.85 (m, 6H; *o*-Ph*H*), 8.53 (s, 3H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ 121.1 (s; *o*-Ph), 127.6 (d, ^{2}J(C,P) = 24.0 Hz; PC═*C*H), 129.8 (s; *p*-Ph), 130.2 (s; *m*-Ph), 136.7 (s; *ipso*-Ph), 142.8 (d, ^{1}J(C,P) = 73.7 Hz; P*C*═CH), 196.4 (d, ^{2}J(C,P) = 7.1 Hz; CO_{eq}), 198.8 (d, ^{2}J(C,P) = 24.8 Hz; CO_{ax}). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, CD_2Cl_2): δ 121.2 (s, *o*-Ph), 127.8 (d, ^{2}J(C,P) = 23.4 Hz; PC═*C*H), 129.8 (s, *p*-Ph), 130.3 (s, *m*-Ph), 136.9 (s, *ipso*-Ph), 142.9 (d, ^{1}J(C,P) = 74.4 Hz; P*C*═CH), 196.7 (d, ^{2}J(C,P) = 7.2 Hz; CO_{eq}), 199.1 (d, ^{2}J(C,P) = 24.6 Hz; CO_{ax}). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ −42.3 (s, ^{1}J(P,W) = 257.8 Hz). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, CD_2Cl_2): δ −40.6 (s, ^{1}J(P,W) = 257.2 Hz). IR (KBr): ν 2075 (m, CO_{ax}), 1921 cm^{-1} (s, CO_{eq}). HR FAB-MS: calcd for $C_{29}H_{19}N_9O_5PW$ (M + H) 788.0756, found 788.0776; *m/z* (%) 788 (15) $[M]^+$, 731 (34) $[M - H - 2CO]^+$.

$(OC)_5WP(C_2HN_3Ph)_3Mo(CO)_3$ (8). **7** (98.1 mg, 0.125 mmol) and $(C_7H_8)Mo(CO)_3$[19] (33.9 mg, 0.125 mmol) were taken up in THF (8 mL), with stirring. The resulting bright red solution turned deep red within 10 min, after which the reaction mixture was left standing overnight in the dark at ambient temperature. Subsequently, the glass wall of the reaction vessel was scratched to initiate crystallization, and 1 h later red needles had formed, which were separated from the mother liquor and dried in a stream of N_2 to afford **8**, which still contained 1.58 equiv of THF according to ^{1}H NMR integration (100.6 mg, 74%). The compound slowly decomposes both in the solid state and in solution upon exposure to air but is a stable solid for weeks when stored under N_2 at ambient temperature in the dark. Crystals suitable for X-ray structure determination were obtained by mixing **7** (51.1 mg, 0.065 mmol) and $(C_7H_8)Mo(CO)_3$ (17.7 mg, 0.065 mmol) in THF (5 mL). Mp (sealed capillary): 224 °C dec. ^{1}H NMR (250.1 MHz, CD_2Cl_2): δ 1.82 (m; THF), 3.68 (m; THF), 7.54−7.67 (m, 9H; *m*-Ph*H*, *p*-Ph*H*), 7.71−7.81 (m, 6H; *o*-Ph*H*), 8.59 (s, 3H; ═C*H*). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 25.9 (s; THF), 68.1 (s; THF), 121.9 (s; *o*-Ph), 130.0 (d, ^{2}J(C,P) = 41.1 Hz; PC═*C*H), 130.6 (s; *m*-Ph), 131.6 (s; *p*-Ph), 135.9 (s; *ipso*-Ph), 139.3 (d, ^{1}J(C,P) = 65.5 Hz; P*C*═CH), 194.6 (d, ^{2}J(C,P) = 25.5 Hz; W-CO_{ax}), 195.7 (d, ^{2}J(C,P) = 6.4 Hz; W-CO_{eq}), 227.8 (s; Mo-*C*O). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, CD_2Cl_2): δ −62.8 (s, ^{1}J(P,W) = 261.1 Hz). IR (KBr): ν 2083 (s, W-CO_{ax}), 1999 (sh, W-CO), 1954 (vs, W/Mo-CO), 1907 (vs, W/Mo-CO), 1794 (vs, Mo-CO), 1765 cm^{-1} (vs, Mo-CO). HR FAB-MS: calcd for $C_{32}H_{18}{}^{96}MoN_9O_8P^{184}W$ 966.9581, found 966.9576; *m/z* (%) 969 (73) $[M]^+$, 731 (32) $[M - Mo(CO)_3 - 2\ CO]^+$. Anal.

Calcd for $C_{38}H_{30}MoN_9O_{9.5}PW$ (**8** + 1.5 equiv of THF): C, 42.44; H, 2.81; N, 11.72. Found: C, 41.87; H, 2.87; N, 11.75.

Crystal Structure Determinations. X-ray intensities were measured on a Nonius Kappa CCD diffractometer with a rotating anode (graphite monochromator, $\lambda = 0.710\,73$ Å). The structures were solved with automated Patterson methods[22] and refined with SHELXL-97[23] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[24] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 639631 (**6**), 639632 (**7**), and 639633 (**8**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Data for compound **6**: $C_{24}H_{18}Cl_3N_9OPRh$ + disordered solvent, fw = 688.70,[25] yellow needle, 0.12 × 0.03 × 0.03 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 9.3892(2)$ Å, $b = 16.7894(5)$ Å, $c = 21.7055(7)$ Å, $\beta = 109.1762(10)°$, $V = 3231.78(16)$ Å^3, $Z = 4$, $D_x = 1.415$ g/cm^3,[25] $\mu = 0.86$ mm^{-1}.[25] A total of 22 074 reflections were measured up to a resolution of $((\sin \theta)/\lambda)_{\max} = 0.53$ Å^{-1} at a temperature of 125 K. An absorption correction was not considered necessary. A total of 3940 reflections were unique ($R_{\text{int}} = 0.0614$). The crystal structure contains large voids (754.5 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program,[24] resulting in 197 electrons/unit cell. A total of 352 parameters were refined with no restraints. R1/wR2 ($I > 2\sigma(I)$): 0.0375/0.0899. R1/wR2 (all reflections): 0.0529/0.0942. $S = 1.013$. The residual electron density was between −0.55 and 0.60 e/Å^3.

Data for compound **7**: $C_{29}H_{18}N_9O_5PW \cdot C_4H_8O$, fw = 859.45, yellow needle, 0.18 × 0.09 × 0.06 mm^3, monoclinic, $C2/c$ (No. 15), $a = 27.6093(5)$ Å, $b = 20.4105(5)$ Å, $c = 13.53985(18)$ Å, $\beta = 114.452(1)°$, $V = 6945.6(2)$ Å^3, $Z = 8$, $D_x = 1.644$ g/cm^3, $\mu = 3.43$ mm^{-1}. A total of 78 673 reflections were measured up to a resolution of $((\sin \theta)/\lambda)_{\max} = 0.65$ Å^{-1} at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.56−0.81 correction range). A total of 7986 reflections were unique ($R_{\text{int}} = 0.0771$). A total of 451 parameters were refined with no restraints. R1/wR2 ($I > 2\sigma(I)$): 0.0331/0.0576. R1/wR2 (all reflections): 0.0623/0.0651. $S = 1.031$. The residual electron density was between −0.89 and 1.08 e/Å^3.

Data for compound **8**: $C_{32}H_{18}MoN_9O_8PW \cdot C_4H_8O$ + disordered solvent, fw = 1039.4,[25] red plate, 0.30 × 0.18 × 0.06 mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 10.87209(6)$ Å, $b = 17.3152(2)$ Å, $c = 29.6070(6)$ Å, $\beta = 98.052(1)°$, $V = 5518.65(14)$ Å^3, $Z = 4$, $D_x = 1.251$ g/cm^3,[25] $\mu = 2.39$ mm^{-1}.[25] A total of 103 081 reflections were measured up to a resolution of $((\sin \theta)/\lambda)_{\max} = 0.65$ Å^{-1} at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.18−0.43 correction range). A total of 12 685 reflections were unique ($R_{\text{int}} = 0.0567$). The crystal structure contains large voids (2136 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program,[24] resulting in 440 electrons/unit cell. A total of 514 parameters were refined with no restraints. R1/wR2 ($I > 2\sigma(I)$): 0.0313/0.0747. R1/wR2 (all reflections): 0.0410/0.0773. $S = 1.086$. The residual electron density was between −0.94 and 1.39 e/Å^3.

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Supporting Information Available: Figures giving the NMR spectra of all new compounds and CIF files giving crystallographic data for **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Derived values do not contain the contribution of the disordered solvent molecules.