Dinuclear Potassium-Chromium and Potassium-Tungsten Carbonyl Complexes

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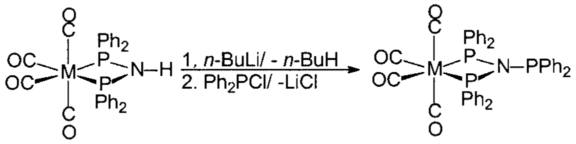
The tetracarbonyl complexes [M(CO)$_4${η^2-(Ph$_2$P)$_2$NH}] [M = Cr (**1a**), W (**1b**)] have been synthesised by reaction of M(CO)$_6$, Me$_3$NO·2H$_2$O, and (Ph$_2$P)$_2$NH. Subsequent treatment of complexes **1a**,**b** with an excess of KH in THF at room temperature yields the potassium salts [Cr(CO)$_4${η^2-(Ph$_2$P)$_2$N}K(THF)$_3$]$_n$ (**2a**) and [W(CO)$_4${η^2-(Ph$_2$P)$_2$N}K(THF)$_2$]$_n$ (**2b**), respectively, in almost quantitative yields. The ionic compounds **2a**,**b** are stable at room temperature. All four compounds **1a**,**b** and **2a**,**b** were characterised by single-crystal X-ray diffraction. Compounds **2a**,**b** form infinite chains via isocarbonyl bridges in the solid state.

Introduction

Anionic P−N systems such as phosphinimides (R$_2$PNR′),[1,2] diphosphinoamides [(Ph$_2$P)$_2$N],[3−6] phosphoraneiminates (R$_3$PN),[7−9] phosphiniminomethanides [(RNPR′$_2$)CH],[10] phosphiniminomethandiides [(RNPR′$_2$)C][11] and diiminophoshphinates [(R$_2$P(NR′)][12] have been known for a long time and their chemistry has been intensively studied over the years. Today there are numerous papers describing the synthesis, structure and reactivity of these anions.[13] The P−N anions are frequently used as ligands in main group and transition metal chemistry.[7,14−16] Even sodium and potassium have sometimes been used as counterions for the P−N anions, although the vast majority of these compounds are lithium salts. These alkali-metal salts are generally generated by deprotonation of the corresponding neutral P−N system, for example an aminophosphane, with butyllithium,[1] sodium[4] or potassium hydride,[6] KO*t*Bu,[5] or by other methods.[8] Ellermann et al. have reported the deprotonation of a neutral P−N ligand that is coordinated to a transition metal fragment.[17,18] This work was performed in situ by deprotonation of bis(diphenylphosphanyl)aminechromium, -molybdenum or -tungsten tetracarbonyl, [M(CO)$_4${η^2-(Ph$_2$P)$_2$NH}] (M = Cr, Mo, W) with *n*-butyllithium. Due to its high sensitivity towards moisture and air the obtained intermediate was not isolated or characterised but further reacted at dry-ice temperature with, for example, chlorophosphanes (Scheme 1). A similar reaction has been performed on metal clusters having the (Ph$_2$P)$_2$NH ligand in the coordination sphere.[19] Again, the corresponding alkali metal species was not isolated. Other groups have reported the deprotonation of cationic complexes ligated by (Ph$_2$P)$_2$NH, which led to zwitterionic compounds.[20]



Scheme 1

In this article we report on the synthesis and structural characterisation of bis(diphenylphosphanyl)aminechromium and -tungsten tetracarbonyl, [M(CO)$_4${η^2-(Ph$_2$P)$_2$NH}] [M = Cr (**1a**), W (**1b**)], along with details of further reactions of these complexes with potassium hydride. These reactions lead, in a deprotonation reaction, to the corresponding amidopotassium compounds [M(CO)$_4${η^2-(Ph$_2$P)$_2$N}K(THF)$_x$]$_n$ [M = Cr (**2a**), W (**2b**); x = 2, 3], which have been isolated and fully characterised by standard analytical/spectroscopic techniques. The structures of **2a**,**b** have been confirmed by single-crystal X-ray diffraction in the solid state. Compounds **2a**,**b** form infinite chains via isocarbonyl bridges in the solid state.

Results and Discussion

Synthesis

The tetracarbonyl complexes [M(CO)$_4${η^2-(Ph$_2$P)$_2$NH}] [M = Cr (**1a**), W (**1b**)] have been synthesised previously by reaction of M(CO)$_6$ with (Ph$_2$P)$_2$NH in boiling dodecane.[18,21] We made compounds **1a**,**b** by reaction of M(CO)$_6$, Me$_3$NO·2H$_2$O, and (Ph$_2$P)$_2$NH in good yield at room temperature (Scheme 2). Compound **1a** was obtained without significant amounts of by-product, whereas the synthesis of **1b** also yielded the pentacarbonyl complex [W(CO)$_5${η^1-(PhP$_2$)$_2$NH}]. Both **1a** and **1b** were character-

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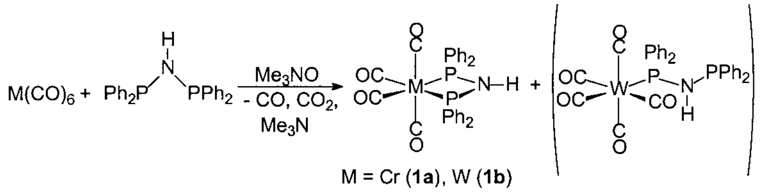
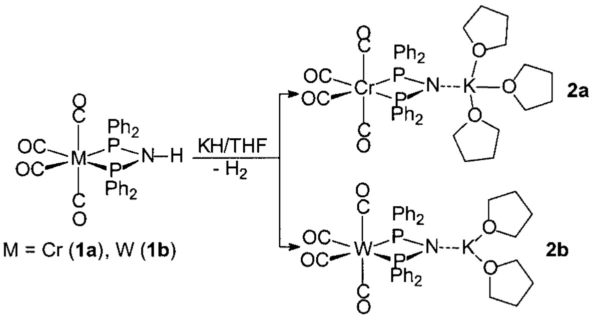


Scheme 2

ised by standard spectroscopic techniques. The observed chemical shifts in the NMR spectra are in good agreement with the literature data.[18,21]

The solid-state structures of both compounds were established by single-crystal X-ray diffraction in order to learn how further reactions at the ligand alter the complex framework.

The potassium salts [Cr(CO)$_4${η^2-(Ph$_2$P)$_2$N}K(THF)$_3$]$_n$ (**2a**) and [W(CO)$_4${η^2-(Ph$_2$P)$_2$N}K(THF)$_2$]$_n$ (**2b**) were obtained in almost quantitative yield by treatment of the neutral complexes **1a**,**b** with an excess of KH in THF at room temperature (Scheme 3). The ionic compounds **2a**,**b** are stable at room temperature even after several weeks the only sign of decomposition in the solid state is the loss of THF from the crystals. In solution we did not observe a possible intermolecular reaction of the amido group with the carbonyl ligand.



Scheme 3

Compounds **2a** and **2b** were characterised by Raman, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy and elemental analysis. The ^{31}P{^{1}H} NMR resonances of **2a**,**b** [δ = 58.7 ppm (**2a**), 8.07 ppm (**2b**)] are significantly shifted upfield relative to **1a**,**b** [δ = 96.9 ppm (**1a**), 46.1 ppm (**1b**)]. Furthermore, an expected $^{1}J_{P,W}$ coupling in **2b** of 168.7 Hz is observed, which is about 40 Hz smaller than in **1b**. Based on earlier measurements of (Ph$_2$P)$_2$CH$_2$ and [M(CO)$_4${η^2-(Ph$_2$P)$_2$CH$_2$}] the signals in the ^{13}C{^{1}H} NMR spectra could be clearly assigned in the phenyl and in the carbonyl region.[22]

Solid-State Structures

The solid-state structures of **1a**,**b** (Figures 1 and 2, respectively) and **2a**,**b** (Figures 3 and 4, respectively) were established by single-crystal X-ray diffraction. The bond lengths and angles of **1a**,**b** are in the expected range. The complex framework is similar to the structurally characterised molybdenum compound [Mo(CO)$_4${η^2-(Ph$_2$P)$_2$NH}]·CH$_3$CN.[23] In contrast to compound **1a**, in **1b** one molecule of acetone is bound via a hydrogen bond to the N−H function of the ligand.

The ionic complexes **2a**,**b** show some surprising aspects in the solid state. Both complexes form polymeric one-dimensional chains in the crystal. In Figure 5 a cutout of the infinite chain of **2a** is shown. The potassium cations are bound to the amido nitrogen atom of one anion and to the oxygen atom of a carbonyl group of a neighbouring anion. Thus, a potassium isocarbonyl compound is formed. The K−N bond lengths are 271.1(2) pm (**2a**) and 273.6(3) pm (**2b**) and the K−O bond lengths are 264.9(2) pm (**2a**) and 270.2(3) pm (**2b**). There are no other structurally characterised K−W and only a few K−Cr isocarbonyl complexes

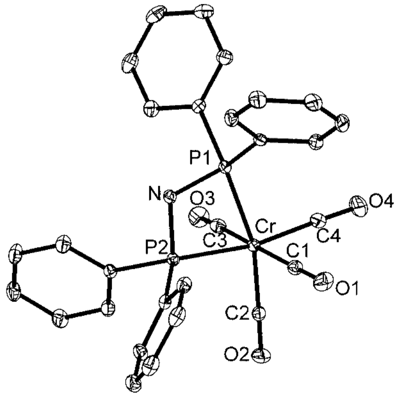


Figure 1. Perspective ORTEP view of the molecular structure of **1a**; thermal ellipsoids are drawn to encompass 50% probability; hydrogen atoms are omitted for clarity; selected distances [pm] and angles [°]: Cr−C1 189.1(2), Cr−C2 189.6(2), Cr−C3 185.2(2), Cr−C4 186.4(2), Cr−P1 236.33(6), Cr−P2 234.50(6), N−P1 169.6(2), N−P2 168.8(2), O1−C1 114.4(2), O2−C2 113.9(2), O3−C3 115.7(2), O4−C4 115.0(2); C1−Cr−C2 174.18(9), C1−Cr−C3 90.39(9), C1−Cr−C4 86.62(9), C2−Cr−C3 86.08(9), C2−Cr−C4 89.08(9), C3−Cr−C4 95.18(9), C1−Cr−P1 92.34(6), C2−Cr−P1 92.25(6), C3−Cr−P1 165.00(6), C4−Cr−P1 99.70(7), C1−Cr−P2 92.66(7), C2−Cr−P2 92.35(6), C3−Cr−P2 96.57(6), C4−Cr−P2 68.23(7), P1−Cr−P2 68.58(2), P1−N−P2 103.24(9)

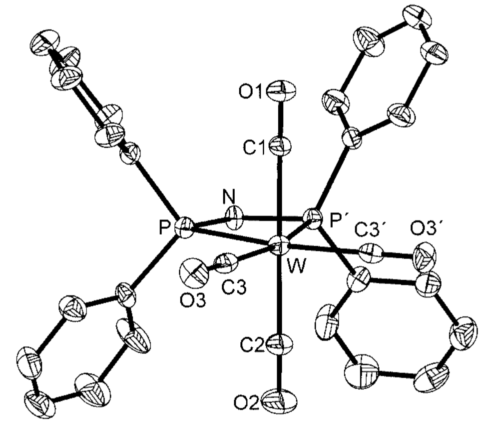


Figure 2. Perspective ORTEP view of the molecular structure of **1b**; thermal ellipsoids are drawn to encompass 50% probability; hydrogen atoms are omitted for clarity; selected distances [pm] and angles [°]: W−C1 205(2), W−C2 200(2), W−C3 201.4(15), W−P 249.2(4), N−P 167.3(10), O1−C1 113(2), O2−C2 118(3), O3−C3 114(2); C1−W−C2 176.8(9), C1−W−C3 87.6(6), C2−W−C3 90.3(6), C3−W−C3′ 97.9(8), C1−W−P 92.3(5), C2−W−P 90.3(6), C3−W−P 98.7(4), C1−W−P′ 92.3(5), C2−W−P′ 90.3(6), C3−W−P′ 163.4(4), P−W−P′ 64.7(2), P−N−P′ 105.7(9)

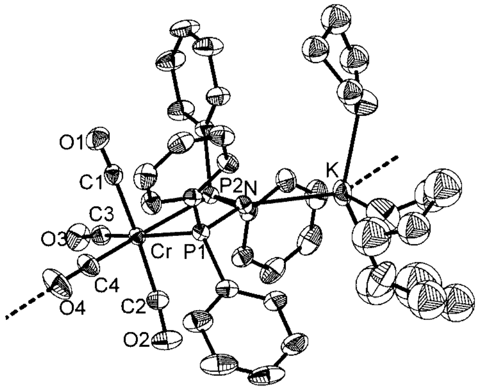


Figure 3. Perspective ORTEP view of the molecular structure of **2a**; thermal ellipsoids are drawn to encompass 50% probability; hydrogen atoms are omitted for clarity; selected distances [pm] and angles [°]: Cr−C1 189.2(2), Cr−C2 188.0(2), Cr−C3 185.5(2), Cr−C4 182.2(2), Cr−P1 236.74(7), Cr−P2 239.80(6), P1−N 166.4(2), P2−N 167.3(2), C1−O1 114.2(3), C2−O2 114.2(3), C3−O3 115.8(3), C4−O4 116.4(3), K−N1 271.1(2), K−O4′ 264.9(2), K−O5 266.8(3), K−O6 266.3(3), K−O7 270.3(3); C1−Cr−C2 174.72(10), C1−Cr−C3 93.88(10), C1−Cr−C4 88.46(11), C2−Cr−C3 88.55(10), C2−Cr−C4 86.68(11), C3−Cr−C4 94.07(11), C1−Cr−P1 90.05(7), C2−Cr−P1 88.86(7), C3−Cr−P1 164.31(7), C4−Cr−P1 101.23(8), C1−Cr−P2 87.50(7), C2−Cr−P2 96.63(7), C3−Cr−P2 101.53(7), C4−Cr−P2 164.12(8), P1−Cr−P2 63.43(2), O4′−K−O5 74.58(8), O4′−K−O6 115.56(10), O4′−K−O7 85.35(10), O4′−K−N 130.54(8), P1−N−P2 97.30(9), P1−N−K 138.73(9), P2−N−K

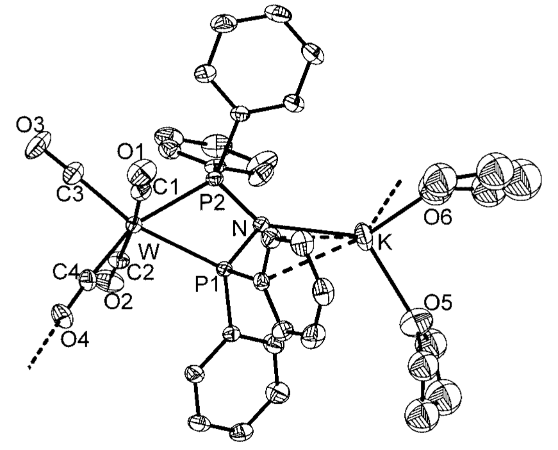


Figure 4. Perspective ORTEP view of the molecular structure of **2b**; thermal ellipsoids are drawn to encompass 50% probability; hydrogen atoms are omitted for clarity; selected distances [pm] and angles [°]: W−C1 202.3(4), W−C2 202.0(4), W−C3 200.2(4), W−C4 196.0(4), W−P1 251.80(8), W−P2 254.20(9), P1−N 166.0(3), P2−N 167.1(3), C1−O1 114.5(5), C2−O2 114.2(5), C3−O3 113.9(5), C4−O4 117.3(5), K−N1 273.6(3), K−O4′ 270.2(3), K−O5 260.4(6), K−O6 255.0(7); C1−W−C2 174.16(15), C1−W−C3 87.0(2), C1−W−C4 89.7(2), C2−W−C3 90.03(2), C2−W−C4 85.56(15), C3−W−C4 94.5(2), C1−W−P1 94.23(12), C2−W−P1 89.99(12), C3−W−P1 164.14(14), C4−W−P1 101.34(11), C1−W−P2 96.49(12), C2−W−P2 89.10(11), C3−W−P2 103.78(14), C4−W−P2 160.99(11), P1−W−P2 60.37(3), O4′−K−O5 94.85(15), O4′−K−O6 82.4(2), O4′−K−N 92.24(10), P1−N−P2 99.62(14), P1−N−K 107.04(12), P2−N−K 142.99(15)

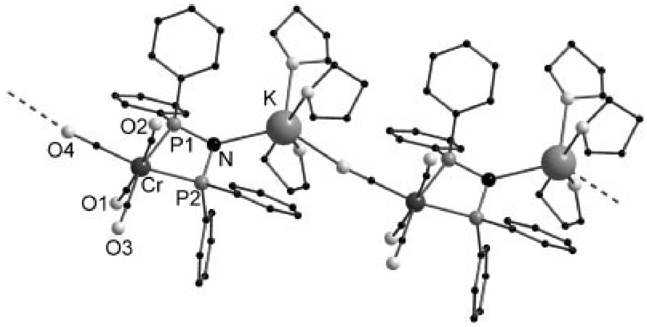


Figure 5. Solid-state structure of **2a** showing the atom labelling scheme, omitting hydrogen atoms; two units of infinite chain are shown

reported in the literature.[24] Furthermore, in **2a** the potassium atom is coordinated by three THF molecules and no π-coordination of the phenyl rings is observed. In contrast, the potassium atom of compound **2b** is surrounded by only two THF molecules. Due to the vacant coordination sites π-coordination of one phenyl ring of the $(Ph_2P)_2N$ group is seen. The different coordination modes of the potassium atoms in **2a** and **2b** cause significantly different O−K−N bond angles [130.54(8)° (**2a**) and 92.24(10)° (**2b**)] in both compounds. Furthermore, the M−C and the C−O bond lengths are also influenced. In the CO group (C4O4) that forms the isocarbonyl bridge in **2a**,**b**, the M−C bond lengths are shortened, whereas the C−O bond lengths are lengthened [M−C: 186.4(2) pm (**1a**), 201.4(15) pm (**1b**), 182.2(2) pm (**2a**), 196.0(4) pm (**2b**); C−O: 115.0(2) pm (**1a**), 114(2) pm (**1b**), 116.4(3) pm (**2a**), 117.3(5) pm (**2b**)].

Due to the deprotonation of the $(Ph_2P)_2NH$ ligand in **2a**,**b** the geometry of the $(Ph_2P)_2N$ group is significantly different to that in **1a**,**b**. The P−N−P angles of **2a**,**b** [97.30(9)° (**2a**) and 99.62(14)° (**2b**)] are narrower than in $(Ph_2P)_2NH$ [118.9(2)°][25] and **1a**,**b** [103.24(9)° (**1a**) and 105.7(9)° (**1b**)]. The P−N distances of **2a**,**b** [166.4(2) pm, 167.3(2) pm (**2a**); 166.0(3) pm 167.1(3) pm (**2b**)], are slightly shorter than those observed in **1a**,**b** [169.6(2) pm, 168.8(2) pm (**1a**); 167.3(10) pm (**1b**)] and $(Ph_2P)_2NH$ (168.2 pm). All the P−N distances indicate a partial P−N multiple-bond character.[1a] Since the deprotonation does not significantly influence the P−N bond length we suggest that the negative charge in **2a**,**b** is basically located on the nitrogen atom. This is supported by the N−K contact in the solid state. To the best of our knowledge only three other structurally characterised heterobimetallic transition metal−alkali metal P−N complexes have been reported in the literature,[26] and none of them was generated by deprotonation of the corresponding phosphinoamine compound.

The Raman spectra of compounds **1a**,**b** and **2a**,**b** were recorded in the solid state. The spectrum of **1b** (without acetone) has been reported previously.[18] For **1b** we observe the same number of vibration modes, but at slightly different wavenumbers. This may be a result of the additional molecule of acetone. Based on earlier measurements on $[M(CO)_4\{\eta^2\text{-}(Ph_2P)_2CH_2\}]$ (M = Cr, W) the vibration modes could be clearly assigned.[27] For the C−O stretching vibration in **2a**,**b** a noticeable shift to lower wavenumbers is seen. This effect is especially noticeable for the symmetric and asymmetric stretching vibration of the equatorial CO groups (up to 56 cm^{-1} for **2a**). The weakening of the C−O bond observed in the Raman spectra is in agreement with the data of the single-crystal X-ray structures.

Conclusions

The $(Ph_2P)_2N^-$ anion, which was previously generated by a deprotonation reaction of $(Ph_2P)_2NH$, has been used to build alkali metal[3−6] titanium,[28] lanthanide,[6] and late transition metal complexes and clusters.[19,20] Now we have shown that the deprotonation of the tetracarbonyl complexes $[M(CO)_4\{\eta^2\text{-}(Ph_2P)_2NH\}]$ (M = Cr, W) with potassium hydride leads to bimetallic amidopotassium−isocarbonyl complexes $[Cr(CO)_4\{\eta^2\text{-}(Ph_2P)_2N\}K(THF)_3]_n$ (**2a**) and $[W(CO)_4\{\eta^2\text{-}(Ph_2P)_2N\}K(THF)_2]_n$ (**2b**), in which the transition metal is bound to the phosphorous atom and the alkali metal is coordinated to the nitrogen atom. Complexes **2a**,**b** form polymeric one-dimensional chains in the solid state. The new amido compounds are stable at room temperature and no intermolecular reaction of the amido function with carbonyl group is observed. Based on the results of the single-crystal X-ray structures we suggest that the negative charge is basically localised on the nitrogen atom.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} Torr) line, or in an argon-filled M. Braun glove box. Ether solvents (tetrahydrofuran and diethyl ether) were predried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum-line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. CH_2Cl_2 and CH_3CN were distilled from over P_2O_5. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom% D). NMR spectra were recorded on a Jeol JNM-LA 400 FT NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (^1H and ^{13}C) or 85% phosphoric acid (^{31}P NMR). Raman spectra were performed on a Bruker RFS 100. Elemental analyses were carried out with an Elementar vario EL. $(Ph_2P)_2NH$ was prepared according to a literature procedure.[29]

$[Cr(CO)_4\{\eta^2\text{-}(Ph_2P)_2NH\}]$ (1a): a) A solution of $Me_3NO{\cdot}2H_2O$ (1.14 g) in 11 mL of MeOH was added dropwise over 3 h to a suspension of $(Ph_2P)_2NH$ (1.78 g, 4.62 mmol) and $Cr(CO)_6$ (1.08 g, 4.91 mmol) in 25 mL of CH_2Cl_2. After this time the reaction mixture was stirred at room temperature for 18 h, filtered through silica gel and the solvents evaporated under reduced pressure. The solid residue was crystallised from hexane/CH_2Cl_2 mixture. Yield: 2.15 g (84.6%).
b) Upon addition of $Me_3NO{\cdot}2H_2O$ (0.23 g, 2.07 mmol) to a suspension of $Cr(CO)_6$ (0.42 g, 1.9 mmol) in 30 mL of MeCN at 0 °C, a yellow colour steadily developed. After 10 min of vigorous stirring, solid $(Ph_2P)_2NH$ (0.75 g; 1.95 mmol) was added to the reaction mixture. The resulting solution was stirred for 18 h at room temperature and then at 70 °C for 5 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using hexane/acetone (4:1) as eluent. The bright-yellow fraction ($R_f \approx 0.3$) was isolated and recrystallised from hexane/CH_2Cl_2 mixture. Yield: 0.63 g (60.3%). Raman (solid): $\tilde{\nu} = 3323$ cm^{-1} (w, νN−H), 3058 (m, νC=C-*H*), 2018 (m, νCO_{ax}), 1915 (m, $\nu_{sym}CO_{eq}$), 1859 (m, $\nu_{asym}CO_{eq}$), 1583 (w, νC=C), 998 (s, νPC), 644 (w, δCO), 470 (m, νMC), 415 (m, νMC), 187 (s, νMP). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 7.51-7.23$ (m, 20 H, Ph), 4.88 (t, $^2J_{P,H} = 6.9$ Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): $\delta = 228.8$ (t, $^2J_{P,C} = 8.7$ Hz, CO_{ax}), 221.7 (t, $^2J_{P,C} = 13.2$ Hz, CO_{eq}), 139.3 (m, $J_{P,C} = 19.9$ Hz, C_{ipso}), 130.5 (s, C_{para}), 130.3 (m, $^2J_{P,C} = 6.6$ Hz, C_{ortho}), 128.7 (m, $J_{P,C} = 4.9$ Hz, C_{meta}) ppm. ^{31}P NMR ($CDCl_3$, 161.7 MHz, 25 °C): $\delta = 96.9$ ppm. $C_{28}H_{21}CrNO_4P_2$ (549.47) C 61.21, H 3.85, N 2.55; found C 60.99, H 3.80, N 2.43.

$[W(CO)_4\{\eta^2\text{-}(Ph_2P)_2NH\}]$ (1b) and $[W(CO)_5\{\eta^1\text{-}(Ph_2P)_2NH\}]$: A mixture of $W(CO)_6$ (2.7 g, 7.67 mmol), $Me_3NO{\cdot}2H_2O$ (0.86 g, 7.75 mmol), and $(Ph_2P)_2NH$ (2.86 g, 7.43 mmol) in 100 mL of MeCN was stirred at room temperature for 20 h and then heated at 60 °C for 18 h. The resulting yellow-green solution was evaporated to dryness and the residue was chromatographed on silica gel using hexane/acetone/ethyl acetate (4:1:1) as eluent. The colourless ($R_f \approx 0.7$) and bright-yellow ($R_f \approx 0.7$) fractions were isolated. Recrystallisation of the first fraction from hexane/acetone gave $[W(CO)_5\{\eta^1\text{-}(Ph_2P)_2NH\}]{\cdot}Me_2CO$ (0.9 g, 17.1%). A second fraction was recrystallised from hexane/ethyl acetate. The obtained crystals were dissolved in toluene and the solution was evaporated in vacuo to give $[W(CO)_4\{\eta^2\text{-}(Ph_2P)_2NH\}]$.
1b: Yield: 2.52 g (49.8%). Raman (solid, **1b**·acetone): $\tilde{\nu} = 3054$ cm^{-1} (m, νC=C-*H*), 2018 (m, νCO_{ax}), 2923 (m, νCH), 1896 (m, νCO), 1884 (m, νCO), 1872 (m, νCO), 1859 (m, νCO), 1699 (m, νCO), 1586 (w, νC=C), 998 (s, νPC), 456 (sh νMC), 441 (sh, νMC), 180 (s, νMP). ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 7.46$ (m, 8 H), 6.95 (m, 12 H, Ph), 5.13 (t, $^2J_{P,H} = 5$ Hz, 1 H, NH) ppm. ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): $\delta = 210.7$ (dd, $^2J_{P,C} = 22.7$ Hz and 7.0 Hz, CO_{eq}), 202.7 (t, $^2J_{P,C} = 7.0$ Hz, CO_{eq}), 138.6 (dd, $^1J_{P,C} = 38.2$ Hz; $^3J_{P,C} = 6.8$ Hz, C_{ipso}), 130.7 (d, $^2J_{P,C} = 15.6$ Hz, C_{ortho}), 130.6 (s, C_{para}), 128.7 ($^2J_{P,C} = 4.9$ Hz, C_{meta}) ppm. ^{31}P NMR (C_6D_6, 161.7 MHz, 25 °C): $\delta = 46.1$ (s, $^1J_{P,W} = 208.1$ Hz) ppm.

$W(CO)_5\{\eta^1\text{-}(Ph_2P)_2NH\}$: ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ = 7.55 (m), 7.26 (m), 6.91 (m) (20 H, Ph); 3.48 (t, $^2J_{P,H}$ = 6.5 Hz, 1 H, NH), 1.54 (s, 6 H, Me_2CO) ppm. ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ = 203.9 ($Me_2\mathit{C}O$), 199.8 (d, $^2J_{P,C}$ = 23.2 CO_{trans}), 197.6 (dd, $^2J_{P,C}$ = 7.83, $^4J_{P,C}$ = 2.9 Hz, CO_{cis}), 141.0 (dd, $^1J_{P,C}$ = 15.1, $^3J_{P,C}$ = 6.0 Hz), 139.1 (dd, $^1J_{P,C}$ = 46.5, $^3J_{P,C}$ = 3.9 Hz) (C_{ipso}); 131.7 (dd, $^2J_{P,C}$ = 12.8, $^4J_{P,C}$ = 2.1 Hz), 131.4 (d, $^2J_{P,C}$ = 21.5 Hz) (C_{ortho}); 130.6 (d, $^3J_{P,C}$ = 1.7 Hz), 129.36 (s) (C_{para}); 128.7 (d, $^4J_{P,C}$ = 7.4 Hz), 128.6 (d, $^4J_{P,C}$ = 9.9 Hz) (C_{meta}); 30.1 (Me_2CO) ppm. ^{31}P NMR (C_6D_6, 161.7 MHz, 25 °C): δ = 64.7 (d, $^2J_{P,P}$ = 71, $^1J_{P,W}$ = 267 Hz, coordinated P), 33.84 (d, uncoordinated P).

$[Cr(CO)_4\{\eta^2\text{-}(Ph_2P)_2N\}K(THF)_x]$ ($x = 2-3$) (2a): Solid **1a** (0.50 g, 0.91 mmol) was added to a suspension of KH (70 mg, 1.75 mmol) in 25 mL of THF. After stirring for 4 h at room temperature the solvent was removed in vacuo and the resulting yellow powder was crystallised from THF/*n*-pentane (1:4). After one day yellow crystals were obtained. Yield: 0.69 g (95%). Raman (solid): 3056 cm^{-1} (m, νC=C-*H*), 2983 (w, νCH), 2878 (w, νCH), 1986 (m, νCO_{ax}), 1879 (m, $\nu_{sym}CO_{eq}$), 1802 (m, $\nu_{asym}CO_{eq}$), 1584 (w, νC=C), 998 (s, νPC), 917 (w, νC−C), 483 (m, νMC), 420 (m, νMC), 184 (m, νMP). ^1H NMR ([D_8]THF, 400 MHz, 25 °C): δ = 7.73 (m, 8 H, Ph), 7.17 (m, 8 H, Ph) 7.09 (m, 4 H, Ph), 3.61 (m, 4 H, THF), 1.76 (m, 4 H, THF) ppm. ^{13}C NMR ([D_8]THF, 100.4 MHz, 25 °C): δ = 226.7 (CO_{ax}), 221.4 (t, $^2J_{P,C}$ = 13.2 Hz, CO_{eq}), 149.4 ($J_{P,C}$ = 19.4 Hz, C_{ipso}), 130.7 (s, C_{para}), 130.4 (C_{ortho}), 127.7 ($J_{P,C}$ = 5.8 Hz, C_{meta}), 68.21 (s, THF), 26.36 (s, THF) ppm. ^{31}P NMR ([D_8]THF, 161.7 MHz, 25 °C): δ = 58.7 ppm. $C_{36}H_{36}CrKNO_6P_2$ (x = 2; 731.72): calcd. C 59.09, H 4.96, N 1.91; found C 58.04, H 4.77, N 1.86.

$[W(CO)_4\{\eta^2\text{-}(Ph_2P)_2N\}K(THF)_2]$ (2b): Solid **1b** (2.5 g; 3.67 mmol) was added to a suspension of KH (237 mg, 5.92 mmol) in 50 mL THF. After stirring at room temperature for 4 h the solvent was removed in vacuo and the resulting yellow powder was crystallised from THF/*n*-pentane (1:4). After one day yellow crystals were obtained. Yield: 2.98 g (94%). Raman (solid): $\tilde{\nu}$ = 3055 cm^{-1} (m, νC=C-*H*), 2983 (w, νCH), 2877 (w, νCH), 1997 (m, νCO_{ax}), 1877 (m, $\nu_{sym}CO_{eq}$), 1802 (m, $\nu_{asym}CO_{eq}$), 1584 (w, νC=C), 997 (s, νPC), 918 (w, νC−C), 483 (w, νMC), 442 (m, νMC), 184 (m, νMP). ^1H NMR ([D_8]THF, 400 MHz, 25 °C): δ = 7.69 (m, 8 H, Ph), 7.18 (m, 8 H, Ph) 7.08 (m, 4 H, Ph), 3.61 (m, 4 H, THF), 1.76 (m, 4 H, THF) ppm. ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ = 228.5 (CO_{ax}), 221.63 (CO_{eq}), 148.8 (m, $J_{P,C}$ = 23.09 Hz, C_{ipso}), 127.9 (s, C_{para}), 130.8 (m, $J_{P,C}$ = 6.4 Hz, C_{ortho}), 127.7 (m, $J_{P,C}$ = 5.2 Hz, C_{meta}), 68.2 (s, THF), 26.4 (s, THF). ^{31}P NMR ([D_8]THF, 161.7 MHz, 25 °C): δ = 8.07 ($^1J_{P,W}$ = 168.7 Hz) ppm. $C_{36}H_{36}KNO_6P_2W$ (863.58): calcd. C 50.07, H 4.20, N 1.62; found C 49.95, H 4.17, N 1.54.

X-ray Crystallographic Studies of 1a, 1b, 2a and 2b: Crystals of **1a** and **1b** were obtained from hexane/CH_2Cl_2 and hexane/acetone, respectively. Crystals of **2a** and **2b** were grown from THF/*n*-pentane (1:4). A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fibre. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS or a Bruker CCD SMART 1000 diffractometer. Subsequent computations were carried out on an Intel Pentium III PC.

Data Collection and Refinement: SHELXS-97,[30] SHELXL-97.[31]

1a: Triclinic, space group $P\bar{1}$ (no. 2); lattice constants a = 982.50(14), b = 1160.8(2), c = 1278.0(2) pm, α = 106.368(4)°, β = 94.523(4)°, γ = 113.016(3)°, V = 1257.3(3) × 10^6 pm^3, Z = 2; μ(Mo-K_α) = 0.618 mm^{-1}; $2\theta_{max.}$ = 60.00°; 7271 (R_{int} = 0.0316) independent reflections measured, of which 4618 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.428 and −0.466 e/A^{-3}; 325 parameters (all non-hydrogen atoms were calculated as anisotropic; the positions of the H atoms were calculated for idealised positions) $R1$ = 0.0368; $wR2$ = 0.0874.

1b: Orthorhombic, space group *Pbcm* (no. 57); lattice constants a = 938.84(4), b = 1680.60(7), c = 1920.77(7) pm, V = 3030.6(2) × 10^6 pm^3, Z = 4; μ(Mo-K_α) = 3.956 mm^{-1}; $2\theta_{max.}$ = 56.00°; 3046 (R_{int} = 0.0526) independent reflections measured, of which 2830 were considered observed with $I > 2\sigma(I)$; max. residual electron density 4.760 and −3.408 e/A^{-3}; 183 parameters (all non-hydrogen atoms were calculated as anisotropic; the positions of the H atoms were calculated for idealised positions) $R1$ = 0.0801; $wR2$ = 0.2098.

2a: Monoclinic, space group *Cc* (no. 9); lattice constants a = 1601.3(3), b = 1328.9(3), c = 2056.8(4)pm, β = 111.046(4)°, V = 4084.9(13) × 10^6 pm^3, Z = 4; μ(Mo-K_α) = 0.508 mm^{-1}; $2\theta_{max.}$ = 61.00°; 11604 (R_{int} = 0.0156) independent reflections measured, of which 10574 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.814 and −0.405 e/A^{-3}; 325 parameters (all non-hydrogen atoms were calculated as anisotropic; the positions of the H atoms were calculated for idealised positions) Flack parameter 0.005(13), $R1$ = 0.0403; $wR2$ = 0.1118.

2b: Triclinic, space group $P\bar{1}$ (no. 2); lattice constants a = 969.1(2), b = 1113.5(2), c = 1804.1(3) pm, α = 94.348(3)°, β = 97.122(3)°, γ = 113.016(3)°, V = 108.075(3) × 10^6 pm^3, Z = 2; μ(Mo-K_α) = 3.415 mm^{-1}; $2\theta_{max.}$ = 60.00°; 10514 (R_{int} = 0.0240) independent reflections measured, of which 9368 were considered observed with $I > 2\sigma(I)$; max. residual electron density 2.229 and −1.569 e/A^{-3}; 379 parameters (all non-hydrogen atoms were calculated anisotropic; the positions of the H atoms were calculated for idealised positions) $R1$ = 0.0335; $wR2$ = 0.0975.

CCDC-217820 (**1a**), -217821 (**1b**), -217822 (**2a**), and -217823 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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