



## Research article

Tetracarbonyl group 6B metal complexes of a *N*-(4-acetylphenyl)-*N*-(diphenylphosphino)amine ligand. Molecular structure of *cis*-[Cr(CO)<sub>4</sub>{4-CH<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>-1-N(PPh<sub>2</sub>)<sub>2</sub>}Harbi Tomah Al-Masri<sup>a,\*</sup>, Ziad Moussa<sup>b,\*\*</sup><sup>a</sup> Department of Chemistry, Faculty of Sciences, Al al-Bayt University, P.O. Box 130040, Mafraq, 25113, Jordan<sup>b</sup> Department of Chemistry, College of Science, United Arab Emirates University, P.O. Box 15551, Al Ain, United Arab Emirates

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## ABSTRACT

Chemical reactions of *N*-(4-acetylphenyl)-*N*-(diphenylphosphino)amine ligand (1) with three group 6B metal hexacarbonyls produced *cis*-M(CO)<sub>4</sub>[1- $\eta^2$ -*P,P*][ M = Cr(2), Mo(3), W(4)], respectively. The novel complexes 2–4 were isolated and their structures were elucidated by multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR) and elemental analysis. Crystal-structure determination using single-crystal X-ray diffraction was carried out on complex 2.

## 1. Introduction

The ongoing significance and increasing relevance of amino-phosphine RNH(PR<sub>2</sub>) and bis(phosphino)amine RN(PR<sub>2</sub>)<sub>2</sub> ligands incorporating direct P–N bonds and their analogues in catalysis and coordination chemistry has been the subject of several review articles [1, 2, 3, 4, 5, 6, 7, 8]. The synthesis of polydentate aminophosphine ligands bearing more than one N(PR<sub>2</sub>)<sub>2</sub> unit and their applications have also been reported [9]. Considering bis(phosphino)amines with P–N–P skeletons, coordination occurs mainly through the two phosphorus atoms in  $\eta^2$ -*P,P*, *P*-bidentate mode due to the low basicity of the amine nitrogen caused by the  $\pi$  interaction in the P–N unit [10]. Several bis(phosphino)amine ligands as well as their complexes have been studied in a wide range of catalytic processes [1], particularly in ethylene oligo/polymerization [11] and C–C cross coupling reactions [12]. These ligands are also used as assembling ligands for the formation of multinuclear complexes, due to the multiple donor atoms [13], and some of them and their derivatives have also found applications in surface and materials sciences [14, 15]. Moreover, the chalcogenide forms of this type of ligands are also becoming increasingly important in view of their potential applications in catalysis [16].

In continuation of our work in this research area [17] and to contribute to the interest and need of others [18] in designing amino-phosphines and phosphorus based ligands for transition metal chemistry and catalytic application, herein we report the chemical synthesis and spectroscopic properties of the *cis*-chelate complexes M(CO)<sub>4</sub>[1- $\eta^2$ -*P,P*][ M = Cr(2), Mo(3), W(4)] as well as the crystal structure of 2.

## 2. Results and discussion

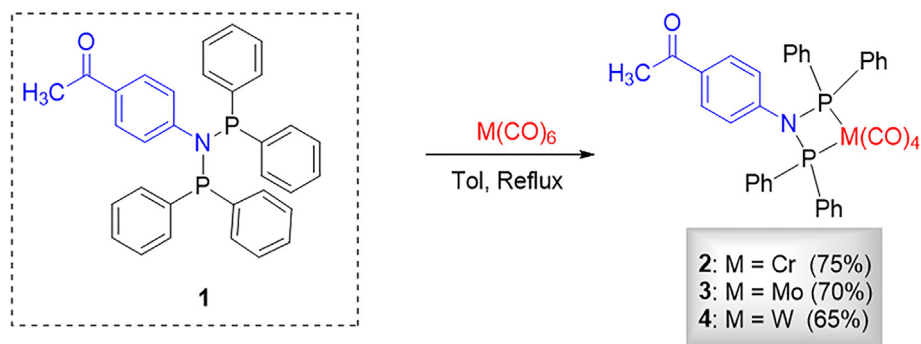
## 2.1. Chemical synthesis of 2–4

Reaction of equimolar amounts of *N*-(4-acetylphenyl)-*N*-(diphenylphosphino)amine ligand [(*p*-CH<sub>3</sub>CO)C<sub>6</sub>H<sub>4</sub>N(PPh<sub>2</sub>)<sub>2</sub>] (1) (see <sup>31</sup>P NMR spectrum of 1-(4-(bis(diphenylphosphanyl)amino)phenyl)ethan-1-one (1) (Fig. S3)) [19], prepared previously from 4-acetylaniline and chlorodiphenylphosphine, with group-6B metal hexacarbonyls in refluxing toluene gave the *cis*-chelate complexes M(CO)<sub>4</sub>[1- $\eta^2$ -*P,P*][ M = Cr(2), Mo(3), W(4)], respectively (Figure 1). The new compounds 2–4 were isolated and structurally elucidated by standard spectroscopic (IR and multinuclear NMR spectroscopy: <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR) and analytical

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [harbialmasri@aabu.edu.jo](mailto:harbialmasri@aabu.edu.jo) (H.T. Al-Masri), [zmoussa@uaeu.ac.ae](mailto:zmoussa@uaeu.ac.ae) (Z. Moussa).



**Figure 1.** Preparation of the *cis*-chelate complexes  $\text{M(CO)}_4[1\text{-}\kappa^2\text{P,P}]$  [M = Cr(2), Mo(3), W(4)].

tools (elemental analysis). The molecular structure of complex **2** has been established crystallographically using single-crystal X-ray diffraction.

## 2.2. Spectroscopic properties

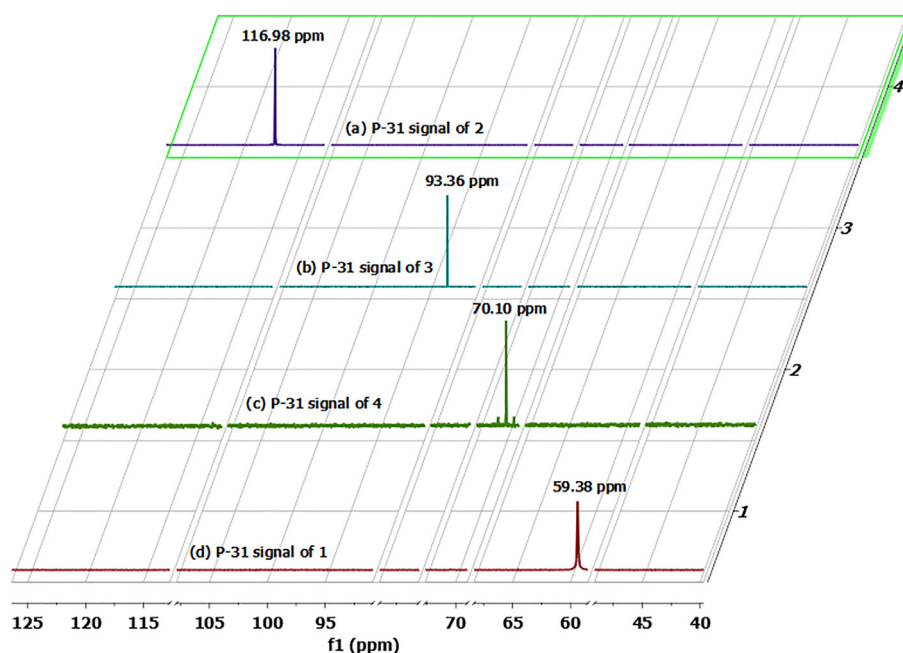
### 2.2.1. $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ NMR, and IR spectra

In the  $^1\text{H}$  NMR spectrum, the acyl group methyl protons comprise the most distinctive signal, appearing as a singlet resonating at  $\delta$  2.41 ppm (**2**) (see  $^1\text{H}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]chromium(0) (**2**) (Fig. S4)), 2.40 ppm (**3**) (see  $^1\text{H}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]molybdenum(0) (**3**) (Fig. S5)), and 2.50 ppm (**4**) (see  $^1\text{H}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]tungsten(0) (**4**) (Fig. S6)). All these signals fall at higher field than those of precursor **1** (2.38 ppm). The  $^1\text{H}$  NMR signals of the aromatic rings of **2-4** fall in the expected chemical shift range ( $\delta$  6.5–7.8 ppm).

The most diagnostic signals in the  $^{13}\text{C}$  NMR spectrum are those related to the acyl group ( $\text{CH}_3$  and  $\text{C}=\text{O}$  carbon atoms). These appear as singlets at  $\delta$  26.3/196.6 (**2**) (see  $^{13}\text{C}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino

amide- $\kappa$ P]chromium(0) (**2**) (Fig. S7)), 25.8/195.0 (**3**) (see  $^{13}\text{C}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]molybdenum(0) (**3**) (Fig. S8)), and 26.0/195.2 (**4**) ppm (see  $^{13}\text{C}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]tungsten(0) (**4**) (Fig. S9)). The  $^{13}\text{C}$  NMR spectra of complexes **2-4** showed two non-equivalent signals for the  $\text{C}\equiv\text{O}$  ligands in agreement with *trans*- and *cis*- $\text{C}\equiv\text{O}$  groups oriented to the P-atoms (see Expanded  $^{13}\text{C}$  NMR spectrum (CO region) of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]chromium(0) (**2**) (Fig. S10) and Expanded  $^{13}\text{C}$  NMR spectrum (CO region) NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]molybdenum(0) (**3**) (Fig. S11)). Also, the  $^{13}\text{C}$  chemical shifts decreased in the order Cr > Mo > W, in parallel with the increasing number of electrons around the metal [17d, 17f].

The  $^{31}\text{P}$  NMR spectra (Figure 2) show one signal at 116.98 ppm (**2**) (Figure 2a) (also see  $^{31}\text{P}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]chromium(0) (**2**) (Fig. S12)), 93.36 ppm (**3**) (Figure 2b)) (also see  $^{31}\text{P}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ P)-*P,P*-diphenylphosphino amide- $\kappa$ P]molybdenum(0) (**3**)).



**Figure 2.** Expanded and truncated  $^{31}\text{P}$  NMR stack spectra (161.98 MHz) for the phosphorus atom resonances for ligand **1** and the corresponding complexes **2-4**. (a)  $^{31}\text{P}$  NMR spectrum for complex **2** (116.98 ppm); (b)  $^{31}\text{P}$  NMR spectrum for complex **3** (93.36 ppm); (c)  $^{31}\text{P}$  NMR spectrum for complex **4** (70.10 ppm ( $^1J_{\text{W-P}} = 207.0$  Hz)); (d)  $^{31}\text{P}$  NMR spectrum for parent ligand **1** (59.38 ppm).

(3) (Fig. S13)), and 70.10 ppm (4) (Figure 2c) (also see  $^{31}\text{P}$  NMR spectrum of *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ -P)-*P*,*P*-diphenylphosphinous amide- $\kappa$ -P] tungsten (0) (4) (Fig. S14)), i.e. shifted downfield relative to the parent organic ligand 1 (59.38 ppm) (Figure 2d) and fall within the same chemical shift range reported for related species described in the literature [1, 17d, 17e, 17f]. The  $^{31}\text{P}$  NMR signal of 4 (Figure 2c) is flanked by two  $^{185}\text{W}$ -satellites with  $^1J_{\text{W-P}}$  coupling constant of 207 Hz, which is in good agreement with structurally-related tungsten complexes [17f].

The IR in the carbonyl region of complexes 2–4 exhibit  $\nu(\text{C}=\text{O})$  bands in the range of 1845–2018  $\text{cm}^{-1}$  typical for *cis*-[ $\text{M}(\text{CO})_4\text{L}_2$ ] [17d, 20].

### 2.3. Molecular structure of 2

Crystals of 2 were obtained as described in the experimental section. Compound 2 crystallizes in the monoclinic space group  $P2_1/n$ . The molecular structure is depicted in Figure 3.

The X-ray structure of 2 contains two crystallographically independent molecules, 2a and 2b (Figure 3), in the asymmetric unit. These differ in the orientation of the phenyl groups. The chromium(0) atom is six coordinated via four terminal carbon monoxide ligands and two phosphorus centers, forming an octahedral geometry. The *P,P*-chelating behavior of ligand 1 to the Cr-metal results in the formation of four-membered ring metallacycle, i.e., P–Mo–P–N (Figure 4), with smaller P–Cr–P [2a: 68.75(3); 2b: 68.98(3)°] bite angle and larger P–N–P [2a: 98.88(9); 2b: 99.23(9)°] bond angle.

A comparison of the structural data of the P–Cr–P and P–N–P bond angles in 2 with the four available literature structural data on analogous *cis*-chelated tetracarbonylchromium(0) *cis*-[Cr(CO) $_4$ {C $_{10}$ H $_7$ -1-N(PPh $_2$ ) $_2$ }] (5) [21], *cis*-[Cr(CO) $_4$ {(o-MeOC $_6$ H $_4$ ) $_2$ P $_2$ NCH $_3$ }] (6) [22], *cis*-[Cr(CO) $_4$ {(Ph $_2$ P) $_2$ N $^t$ Pr}] (7) [23], and *cis*-[Cr(CO) $_4$ {Ph $_2$ P) $_2$ NH}] (8) [24a,b], showed that the P–Cr–P bite angle in 2 [2a: 68.75(3); 2b: 68.98(3)°] is slightly larger than those in 5 [67.54(2)°], 6 [67.54(2)°], 7 [67.82(4)°], 8 [68.58(2)°], and significantly lower than the ideal 90° in a regular square-planar geometry. The P–N–P bond angle in 2 [2a: 98.88(9); 2b: 99.23(9)°] is smaller than those in 5 [100.76(8)°], 6 [101.24(7)°], 8 [103.24(9)°], and slightly similar to these in 7 [99.86(11)°]. The average P–N [av. 1.7291 Å] bond distance in 2 is slightly larger than those in 5 [av. 1.721 Å], 6 [av. 1.699 Å], 7 [av. 1.713 Å], 8 [av. 1.692 Å], and slightly shorter than those in the free diposphinoamine ligands [24, 25] which clearly indicate an enhancement of  $\pi$ -character in the P–N unit. The average Cr–P [av. 2.326 Å] bond distance in 2 is smaller than the corresponding bond lengths found in 5 [av. 2.347 Å], 6 [av. 2.364 Å], 7 [av. 2.350 Å], and 8 [av. 2.354 Å]. It is worth mentioning that the average Cr–C bond distance for C=O groups *trans* to the phosphines is 1.853 Å, whereas those *cis* to phosphines the distance is 1.882 Å. This bond lengthening results from the differing strength of the metal-to-ligand  $\pi$  bonding [21]. The aromatic rings in 2 as expected have usual bond lengths and angles.

## 3. Experimental section

### 3.1. General Remarks

All experimental manipulations were performed under purified dry nitrogen using standard *Schlenk* and vacuum line techniques. Solvents were dried and freshly distilled under an atmosphere of nitrogen prior to use [26]. The chemicals Mo(CO) $_6$ , W(CO) $_6$ , Cr(CO) $_6$ , chlorodiphenylphosphine, and *p*-aminoacetophenone were purchased from Aldrich and used as received. *N*-(4-acetylphenyl)-*N*-(diphenylphosphino) amine ligand (1) was previously prepared [19]. Infra-red spectra were recorded with a PerkinElmer System 2000 FT-IR spectrometer between 4000 and 400  $\text{cm}^{-1}$  using KBr disks. Microanalyses were performed on a Flash 2000 elemental analyzer. Infra-red spectra were recorded on a Shimadzu FTIR-8400S spectrometer between 4000–400  $\text{cm}^{-1}$  using KBr disks. The NMR spectra were recorded at 25 °C on a

*Bruker-Avance-DRX-400* MHz NMR spectrometer operating at 400.17 ( $^1\text{H}$ ), 100.63 ( $^{13}\text{C}$ ), and 161.98 ( $^{31}\text{P}$ ) using tetramethylsilane for  $^1\text{H}$  and 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR as external standards. Melting points were carried out on a *Gallenkamp* apparatus with open capillaries.

### 3.2. Preparation of 2-4

#### 3.2.1. *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ -P)-*P*,*P*-diphenylphosphinous amide- $\kappa$ -P]chromium(0) (2)

A solution of *N*-(4-acetylphenyl)-*N*-(diphenylphosphino)amine ligand (1) (0.70 g, 1.39 mmol) and Cr(CO) $_6$  (0.31 g, 1.39 mmol) was refluxed in 50 mL toluene for 30 h. The solution was reduced under vacuum to 10 mL and the yellow product precipitated by adding 20 mL *n*-hexane. Crystals were obtained from a mixture of  $\text{CH}_2\text{Cl}_2$  \ *n*-hexane at – 4 °C in 75 % yield. Mp 217–220 °C.  $^1\text{H}$  NMR (400.17 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 2.41 (s, 3H,  $\text{CH}_3$ ), 6.66 (d,  $J$  = 8.8 Hz, 2H), 6.65–7.63 (m, 22H,  $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ );  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 26.3 ( $\text{CH}_3$ ), 121.5 (t,  $J_{\text{P-C}}$  = 3.5 Hz), 128.9 (t,  $J_{\text{P-C}}$  = 5.0 Hz), 129.1 (s), 130.9 (t,  $J_{\text{P-C}}$  = 6.5 Hz), 132.1 (s), 135.3 (s) 135.5 (d,  $J_{\text{P-C}}$  = 18.1 Hz), 145.7 (t,  $J_{\text{P-C}}$  = 7.0 Hz) ( $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ ), 196.6 (C=O), 220.9 (t, *cis*-C=O,  $^2J_{\text{P-C}}$  = 12.1 Hz) and 227.8 (t, *trans*-C=O,  $^2J_{\text{P-C}}$  = 9.1 Hz).  $^{31}\text{P}$  NMR (161.97 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 116.98 (s, 2P). Selected IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  (C=O) = 1845,  $\nu$  (C=O) = 1903,  $\nu$  (C=O) = 2013,  $\nu$  (C=O) = 1693. Anal. Calcd. For  $\text{C}_{36}\text{H}_{27}\text{NO}_5\text{P}_2\text{Cr}$ : C 64.77; H 4.08; N 2.10%. Found: C 64.78; H 4.10; N 2.12 %.

#### 3.2.2. *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ -P)-*P*,*P*-diphenylphosphinous amide- $\kappa$ -P]molybdenum(0) (3)

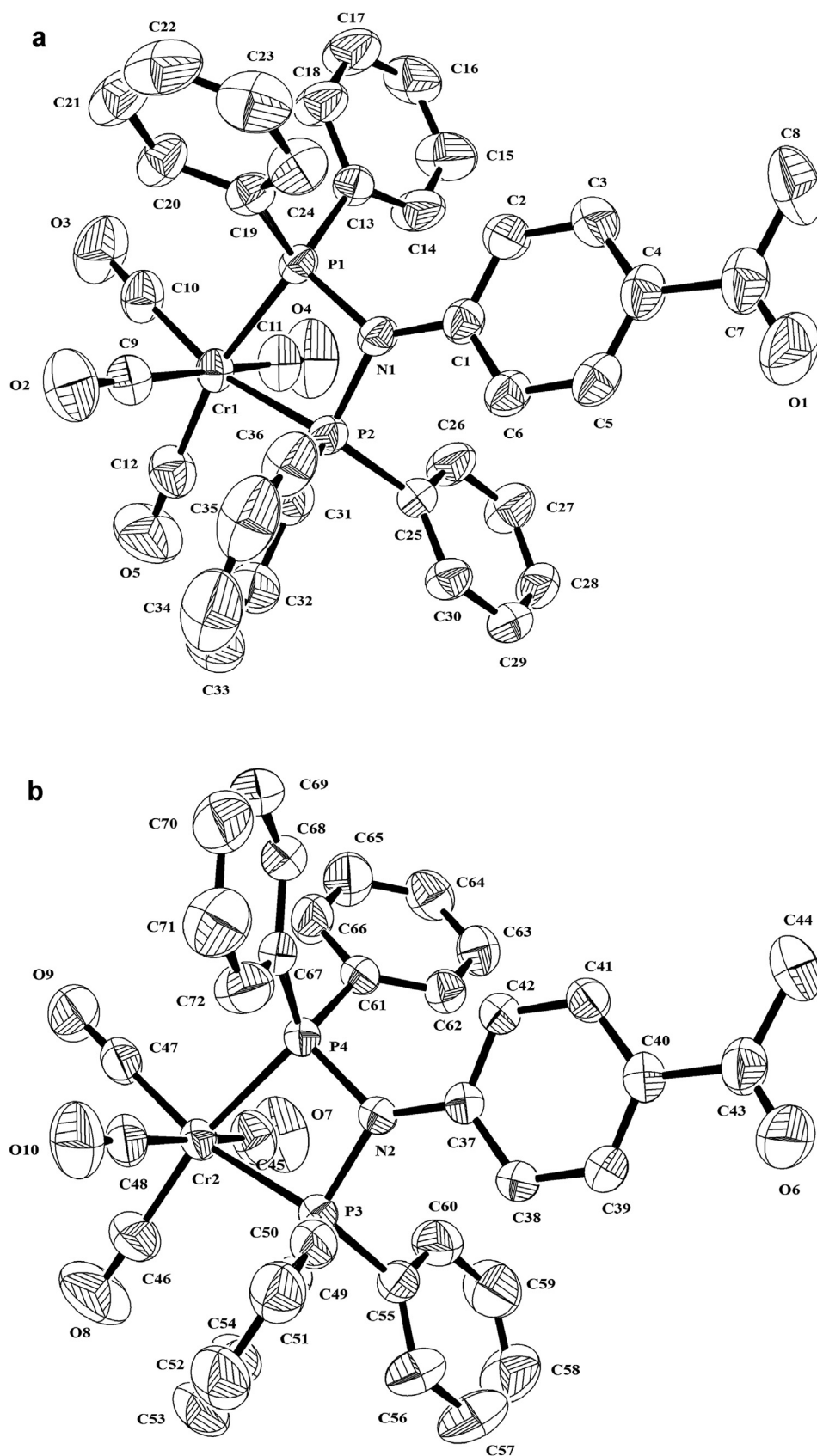
A similar procedure to that described for 2 was used here, except Mo(CO) $_6$  (0.34 g, 1.39 mmol) was employed instead of Cr(CO) $_6$  and the yellow product are obtained in 70% yield. Mp 132–134 °C.  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 2.40 (s, 3H,  $\text{CH}_3$ ), 6.68 (d,  $J$  = 8.8 Hz, 2H), 6.68–7.80 (m, 22H,  $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 25.8 ( $\text{CH}_3$ ), 112.6 (s), 125.0 (s), 127.3 (t,  $J_{\text{P-C}}$  = 5.5 Hz), 127.6 (d,  $J_{\text{P-C}}$  = 11.1 Hz), 129.8 (s), 130.5 (s), 132.1 (t,  $J_{\text{P-C}}$  = 3.0 Hz), 153.2 (s) ( $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ ), 195.0 (C=O), 207.3 (d, *cis*-C=O,  $^2J_{\text{P-C}}$  = 7.1 Hz) and 210.0 (d, *trans*-C=O,  $^2J_{\text{P-C}}$  = 10.1 Hz).  $^{31}\text{P}$  NMR (161.97 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 93.36 (s, 2P). Selected IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  (C=O) = 1850,  $\nu$  (C=O) = 1909,  $\nu$  (C=O) = 2018,  $\nu$  (C=O) = 1692. Anal. calcd. for  $\text{C}_{36}\text{H}_{27}\text{NO}_5\text{P}_2\text{Mo}$ : C 60.77; H 3.82; N 1.97%. Found: C 60.78; H 3.80; N 1.99 %.

#### 3.2.3. *cis*-Tetracarbonyl[*N*-(4-acetylphenyl)-*N*-(diphenylphosphino- $\kappa$ -P)-*P*,*P*-diphenylphosphinous amide- $\kappa$ -P]tungsten(0) (4)

A similar procedure to that described for 2 was used here, except W(CO) $_6$  (0.49 g, 1.39 mmol) was employed instead of Cr(CO) $_6$  and the yellow product are obtained in 65% yield. Mp 162–163 °C.  $^1\text{H}$  NMR (400.17 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 2.50 (s, 3H,  $\text{CH}_3$ ) and 6.56–7.76 (m, 24H,  $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 26.0 ( $\text{CH}_3$ ), 114.2 (s), 127.4 (s), 130.0 (s), 130.4 (s), 132.2 (s), 138.5 (s), 139.2 (s), 150.9 (s) ( $\text{C}_6\text{H}_4$  and  $4\text{C}_6\text{H}_5$ ), 195.2 (C=O), 204.0 (*cis*-C=O) and 206.1 (*trans*-C=O).  $^{31}\text{P}$  NMR (161.97 MHz,  $\text{CDCl}_3$ ,  $\delta$ /ppm): 70.10 (s, 2P,  $^1J_{\text{W-P}}$  = 207.1 Hz). Selected IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  (C=O) = 1860,  $\nu$  (C=O) = 1903,  $\nu$  (C=O) = 2015,  $\nu$  (C=O) = 1695. Anal. calcd. for  $\text{C}_{36}\text{H}_{27}\text{NO}_5\text{P}_2\text{W}$ : C 54.09; H 3.40; N 1.75%. Found: C 54.10; H 3.42; N 1.74 %.

### 3.3. Data collection and structure determination

Crystallographic data are given in Table 1. Single-crystal X-ray diffraction data were collected using an *Oxford Diffraction Supernova* dual-source diffractometer equipped with a 135 mm *Atlas CCD* area detector. Crystals were selected under Paratone-N oil, mounted on micro-mount loops and quench-cooled using an *Oxford Cryosystems* open flow  $\text{N}_2$  cooling device [27]. Data were collected at 150 K using mirror monochromated  $\text{CuK}\alpha$  radiation ( $\lambda$  = 1.5418 Å) and processed using the *CrysAlisPro* package, including unit cell parameter refinement and



**Figure 3.** Molecular structure of the two independent molecules **2a** (above) and **2b** (down) (hydrogen atoms are omitted for clarity). Selected bond distances [Å] and angles [°] **2a**: Cr(1)–C(10) 1.846(3); Cr(1)–C(12) 1.861(3); Cr(1)–C(11) 1.865(3); Cr(1)–C(9) 1.890(3); Cr(1)–C(9) 1.890(3); Cr(1)–P(1) 2.3220(10); Cr(1)–P(2) 2.3270(8); P(1)–N(1) 1.7306(18); P(1)–C(19) 1.821(3); P(1)–C(13) 1.830(2); P(1)–P(2) 2.6249(9); P(2)–N(1) 1.7245(19); P(2)–C(31) 1.823(2); P(2)–C(25) 1.830(2); C(10)–Cr(1)–P(1) 96.50(10); C(12)–Cr(1)–P(1) 164.59(10); C(11)–Cr(1)–P(1) 93.59(10); C(9)–Cr(1)–P(1) 92.93(8); C(10)–Cr(1)–P(2) 165.23(10); C(12)–Cr(1)–P(2) 95.87(10); C(11)–Cr(1)–P(2) 95.07(9); C(9)–Cr(1)–P(2) 92.37(8); P(1)–Cr(1)–P(2) 68.75(3); P(2)–N(1)–P(1) 98.88(9); N(1)–P(1)–C(19) 107.83(11); N(1)–P(1)–C(13) 109.63(10); N(1)–P(1)–Cr(1) 96.01(7); C(19)–P(1)–C(13) 103.08(11); N(1)–P(2)–C(31) 108.65(11); N(1)–P(2)–C(25) 105.46(10); C(31)–P(2)–C(25) 105.55(11); N(1)–P(2)–Cr(1) 96.00(7). Selected bond distances [Å] and angles [°] **2b**: Cr(2)–C(47) 1.840(3); Cr(2)–C(46) 1.866(3); Cr(2)–C(45) 1.876(3); Cr(2)–C(48) 1.895(3); Cr(2)–P(4) 2.3183(8); Cr(2)–P(3) 2.3376(7); P(3)–N(2) 1.7332(19); P(3)–C(49) 1.824(3); P(3)–C(55) 1.829(3); P(3)–P(4) 2.6364(11); P(4)–N(2) 1.7280(18); P(4)–C(61) 1.822(2); P(4)–C(67) 1.829(3); C(47)–Cr(2)–P(4) 97.92(9); C(46)–Cr(2)–P(4) 168.42(10); C(45)–Cr(2)–P(4) 90.92(9); C(48)–Cr(2)–P(4) 93.39(9); C(47)–Cr(2)–P(3) 166.82(9); C(46)–Cr(2)–P(3) 99.49(10); C(45)–Cr(2)–P(3) 94.57(9); C(48)–Cr(2)–P(3) 91.18(8); P(4)–Cr(2)–P(3) 68.98(3); N(2)–P(3)–C(49) 107.41(11); N(2)–P(3)–C(55) 104.93(10); C(49)–P(3)–C(55) 106.35(12); N(2)–P(3)–Cr(2) 95.48(6); N(2)–P(4)–C(61) 107.76(10); N(2)–P(4)–C(67) 105.59(10); C(61)–P(4)–C(67) 105.59(11); N(2)–P(4)–Cr(2) 96.31(7); P(4)–N(2)–P(3) 99.23(9).

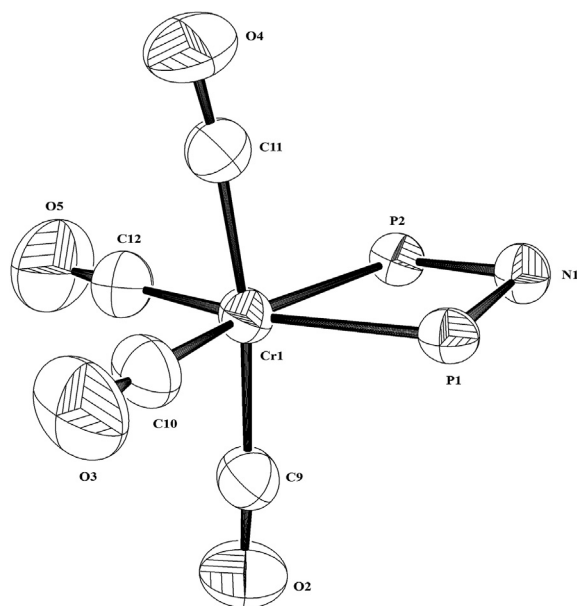


Figure 4. Core center of 2a.

inter-frame scaling (which was carried out using *SCALE3 ABSPACK* within *CrysAlisPro*) [28]. Equivalent reflections were merged and diffraction patterns processed with the *CrysAlisPro*. The structure was subsequently solved using direct methods and refined on  $F^2$  using the *SHELXL* 97-2 package [29]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H-atoms bonded to carbon atoms were placed in geometrically optimized positions and refined with an isotropic displacement parameter relative to the attached atoms. CCDC- 1979888 contains the supplementary crystallographic data (excluding structure factors) for the structure of **2**. These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystal data and structure refinements of **2**.

	2
Formula	$C_{72}H_{54}Cr_2N_2O_{10}P_4$
$M_r$	1335.05
Temp [K]	150(2)
Crystal system	monoclinic
Space group	$P 2_1/n$
$a$ [Å]	13.622(5)
$b$ [Å]	13.060(5)
$c$ [Å]	39.153(5)
$\alpha$ [°]	90
$\beta$ [°]	91.511(5)
$\gamma$ [°]	90
$V$ [Å <sup>3</sup> ]	6963(4)
$Z$	4
$\rho_{\text{calcd}}$ (Mg m <sup>-3</sup> )	1.274
$F(000)$	2752
Abs coeff (mm <sup>-1</sup> )	3.907
No. of rflns coll.	49675
No. of indep rflns	13508
$R_{\text{int}}$	0.0318
No. of parameters	813
$R_1$ ( $I > 2\sigma(I)$ )	0.0390
$wR_2$ (all data)	0.1115
$(\Delta/\rho)_{\text{max}}$ [e.Å <sup>-3</sup> ]	0.276
$(\Delta/\rho)_{\text{min}}$ [e.Å <sup>-3</sup> ]	-0.268

## 4. Conclusion

We have shown the successful synthesis of the *cis*-chelate complexes  $M(\text{CO})_4[1\text{-}r^2\text{-}P,P]$  [ $M = \text{Cr}(2), \text{Mo}(3), \text{W}(4)$ ] and the crystal structure of **2**. The crystallographic study reveals that chromium(0) atom is six coordinated via four terminal carbon monoxide ligands and two phosphorus centers, forming an octahedral geometry. The two Cr–C bonds mutually *trans* are longer than those *trans* to Cr–P bonds due to the various strengths of the metal-to-ligand  $\pi$ -bonding. The above types of complexes are scant in the literature and will be further investigated for their biological properties and synthetic usefulness and will serve as a stepping-stone for further development in the field.

## Declarations

### Author contribution statement

Harbi T. Al-Masri; Ziad Moussa: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Data availability statement

Data will be made available on request.

### Declaration of interests statement

The authors declare no conflict of interest.

### Additional information

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