Research Article

Synthesis and Molecular Structure of *cis*-Tetracarbonyl[*N*-(diphenylphosphino-*kP*)-naphthalen-1-yl-*P,P*-diphenylphosphinous amide-*kP*]chromium(0)

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The reaction of *N,N*-bis(diphenylphosphanyl)naphthylamine $C_{10}H_7-1-N(PPh_2)_2$ with $(C_5H_{10}NH)_2Cr(CO)_4$ (1:1 molar ratio) in dichloromethane afforded *cis*-[Cr(CO)₄{C₁₀H₇-1-N(PPh₂)₂}] (**1**). This complex was crystallized in the monoclinic space group *P*2₁/n. The structure was solved by direct methods and refined by full-matrix least squares techniques to an *R* factor of 0.0313 for 6488 observed reflections. The Cr-metal is coordinated by four terminal CO molecules and a *P,P'*-bidentate *N,N*-bis(diphenylphosphanyl)naphthylamine ligand in a distorted octahedral array. The N-atom adopts a planar geometry with the two P-atoms and C-atom attached to it. The four-membered metallacycle ring P₂CrN is nearly planar.

1. Introduction

As a continuation of our work on the synthesis and solid-state structures of phosphorus(III) ligands containing direct P–N bonds and derivatives [1–4], as these have shown a broad spectrum of anticancer, herbicidal, neuroactive, and antimicrobial activities [5–9], thereof, herein we report the synthesis and crystal structure of *cis*-[Cr(CO)₄{C₁₀H₇-1-N(PPh₂)₂}] (**1**).

2. Materials and Methods

2.1. Chemistry. All experiments were carried out under purified dry nitrogen using standard Schlenk and vacuum line techniques. Solvents were dried and freshly distilled under nitrogen [10]. The chemicals Cr(CO)₆ were used as purchased. C₁₀H₇-1-N(PPh₂)₂ [1] and (C₅H₁₀NH)₂Cr(CO)₄ [11] were prepared according to the literature methods. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer between 4000 and 400 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 (¹H) and 100.63 (¹³C) using tetramethylsilane as external standard.

Melting point was carried out on a Gallenkamp apparatus with open capillaries.

2.2. Preparation of *cis*-Tetracarbonyl[*N*-(diphenylphosphino-*kP*)-naphthalen-1-yl-*P,P*-diphenylphosphinous amide-*kP*]chromium(0) (1**).** A solution of *N,N*-bis(diphenylphosphanyl)naphthylamine (0.26 g, 0.51 mmol) and (C₅H₁₀NH)₂Cr(CO)₄ (0.17 g, 0.51 mmol) in 20 mL of CH₂Cl₂ was refluxed for 2 h. The orange solution was concentrated to ca. 5 mL under reduced pressure, and *n*-hexane (5 mL) was added. Cooling this solution to 0°C gave **3** as yellow crystals in 85% yield. Mp 180–183°C. ¹H NMR (CDCl₃, δ/ppm): 6.40–7.78 (m, 27 H, C₁₀H₇ and 4C₆H₅). ¹³C NMR (CDCl₃, δ/ppm): 124.8, 125.2, 125.6, 125.9, 127.1, 127.9, 128.6, 129.6, 130.5, 131.3, 132.6, 134.1, 135.4, 138.8 (C₁₀H₆ and 4C₆H₅), 221.2 (C ≡ O_{eq}), 228.2 (C ≡ O_{ax}). ³¹P NMR (CDCl₃, δ/ppm): 117.41 (s, 2P). IR (selected bands, KBr, cm^{−1}): ν = 1886 (s, br), 1920 (s), 2008 (s) (C ≡ O).

2.3. 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

TABLE 1: Crystal data and structure refinement for **1**.

Formula	$C_{38}H_{27}CrNO_4P_2$	Z	4
M_r	675.55	$\rho_{\text{calcd}} [\text{Mg m}^{-3}]$	1.342
Temp [K]	150(2)	$F(000)$	1392
Crystal system	Monoclinic	Abs coeff [mm^{-1}]	4.053
Space group	$P2_1/n$	No. of rflns coll.	24513
a [Å]	12.209(5)	No. of indep rflns	6488
b [Å]	20.003(5)	R_{int}	0.0223
c [Å]	13.954(5)	No. of params	415
α [°]	90	$R1 (I > 2\sigma(I))$	0.0313
β [°]	101.085(5)	$wR2$ (all data)	0.0869
γ [°]	90	$(\Delta/\rho)_{\text{max}} [e \cdot \text{\AA}^{-3}]$	0.200
V [Å ³]	3344(2)	$(\Delta/\rho)_{\text{min}} [e \cdot \text{\AA}^{-3}]$	-0.323

a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops, and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device [12]. Data were collected at 150 K using mirror monochromated $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) and processed using the CrysAlisPro package, including unit cell parameter refinement and interframe scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro) [13]. Equivalent reflections were merged and diffraction patterns were processed with the CrysAlisPro. The structure was subsequently solved using direct methods and refined on F2 using the SHELXL 97-2 package [14–16]. All nonhydrogen 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. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-973175 for **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk/>).

3. Results and Discussion

3.1. Synthesis. Complex **1** was previously prepared by the reaction of $\text{Cr}(\text{CO})_6$ with $\text{C}_{10}\text{H}_7\text{-1-N}(\text{PPh}_2)_2$ in refluxing toluene for 36 hours [1]. Here, an alternative synthetic methodology was devised using $(\text{C}_5\text{H}_{10}\text{NH})_2\text{Cr}(\text{CO})_4$ instead of $\text{Cr}(\text{CO})_6$ in refluxing CH_2Cl_2 to avoid prolonged refluxing time and further purification of the desired product. This methodology gave **1** in high yield and without the need for further purification. The NMR data are in agreement with those reported previously in the literature [1].

3.2. Molecular Structure. Yellow colored crystals of **1** were obtained as described in the Experimental Section. **1** crystallizes in the monoclinic space group $P2_1/n$. Selected interatomic distances and angles are collected in Table 2. The molecular structure is depicted in Figure 1.

TABLE 2: Selected bond lengths (Å) and bond angles (deg.) for **1**.

Cr1–C11	1.883(2)	C14–Cr1–C11	175.52(8)
Cr1–C12	1.859(2)	P1–Cr1–C12	100.26(7)
Cr1–C13	1.865(2)	P1–Cr1–C13	166.57(7)
Cr1–C14	1.881(2)	P1–Cr1–C14	88.05(6)
Cr1–P1	2.347(1)	P2–Cr1–C11	93.51(6)
Cr1–P2	2.347(1)	P2–Cr1–C12	168.99(6)
P1–N1	1.719(1)	P2–Cr1–C13	97.99(7)
P2–N1	1.722(1)	P2–Cr1–C14	90.89(6)
P1–C15	1.829(2)	P1–N1–P2	100.70(7)
P1–C21	1.818(2)	P1–Cr1–P2	68.74(3)
P2–C27	1.819(2)	P1–Cr1–C11	92.79(6)
P2–C33	1.830(2)	N1–P1–Cr1	94.26(5)
N1–C1	1.443(2)	N1–P2–Cr1	94.19(5)
C11–O1	1.136(2)	N1–P1–C15	105.49(7)
C12–O2	1.147(2)	N1–P1–C21	109.46(8)
C13–O3	1.140(2)	N1–P2–C27	106.55(8)
C14–O4	1.146(2)	N1–P2–C33	109.00(7)
C12–Cr1–C11	86.43(9)	C15–P1–C21	100.97(8)
C12–Cr1–C13	93.02(9)	C27–P2–C33	101.42(8)
C12–Cr1–C14	89.09(8)	$\sum$ angles at N1	359.91(9)
C13–Cr1–C11	90.05(9)	P2–Cr1–P1–N1	−9.66(5)
C13–Cr1–C14	90.15(9)	C3–C2–C1–N1	−177.61(2)

The crystal structure of **1** shows a distorted octahedral environment around the Cr-metal surrounded by four terminal CO ligands and two phosphorus centers (Figure 1).

The ability of the *N,N*-bis(diphenylphosphanyl)naphthylamine ligand to act as bidentate PP' -chelating ligand to the Cr-metal results in the formation of a four-membered metallacycle, that is, P–Cr–P–N, that is approximately planar with a torsion angle P–Cr–P–N of $-9.66(5)^\circ$, with a smaller P–Cr–P bite angle [$68.74(3)^\circ$] and larger P–N–P bond angle [$100.70(7)^\circ$] (Table 2). The nitrogen atom is displaced out of the plane (Cr1, P1, P2) by $0.2873(14)$ Å.

To the best of our knowledge, there are other three structurally characterized monocyclic four-membered ring complexes of bidentate PP' -chelating bis(phosphino)amine

FIGURE 1: An ORTEP diagram of complex **1** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and arbitrary spheres for the hydrogen atoms.

ligand, namely, *cis*-[Cr(CO)₄{((*o*-MeOC₆H₄)₂P)₂NCH₃}] (**2**) [17], *cis*-[Cr(CO)₄{(Ph₂P)₂N^{*i*}Pr}] (**3**) [18], and *cis*-[Cr(CO)₄{Ph₂P)₂NH}] (**4**) [19].

A comparison of the structural data of the P–Cr–P and P–N–P bond angles in **1** (Table 2) with those of the four-membered rings in similar *cis*-chelated tetracarbonylchromium(0) **2**–**4** shows that the P–Cr–P bite angle in **1** is larger than those in **2** [67.54(2)°], **3** [67.82(4)°], and **4** [68.58(2)°]. The P–N–P bond angle in **1** is smaller than those in **2** [101.24(7)°] and **4** [103.24(9)°] and larger than those in **3** [99.86(11)°].

The P–N–P [100.70(7)°] bond angle is significantly smaller than those in the free diphosphinoamine ligands [19, 20] due to the formation of a strained four-membered chelate ring.

The C-naphthyl skeleton in **1** is almost planar and virtually perpendicular to the P–Cr–P–N plane. A planar environment would be expected for the three-coordinate nitrogen atoms in **1** and the sum of bond angles is indeed close to 360° (Table 2). The P–Cr–C *trans* angles of **1** [166.57(7) and 168.99(6)°] differ significantly from 180°.

The average P–N bond distance in **1** [*av.* 1.721 Å] is slightly longer than those in **2** [*av.* 1.699 Å], **3** [*av.* 1.713 Å], and **4** [*av.* 1.692 Å] and significantly shorter than the sum of Pauling covalent radii (1.77 Å) as expected due to P–N π -bonding. Consistent with this, the nitrogen atom is planar as evidenced by the sum of angles about nitrogen being 359.91(9)° for **1**. Also, the P–N bond distances in **1** are slightly shorter than those in the free diphosphinoamine ligands [19, 20] which clearly indicate an enhancement of π -bonding in the P–N unit.

The two Cr–P bond distances [2.347(1) and 2.347(1) Å] in **1** are equal. The average Cr–P bond distance in **1** [*av.* 2.347 Å] is slightly shorter than those in *cis*-chelated tetracarbonylchromium(0) **2** [*av.* 2.364 Å], **3** [*av.* 2.350 Å], and **4** [*av.* 2.354 Å]. The atoms P1, P2, Cr1, C12, and C13 are essentially coplanar with a maximum deviation from the mean plane of 0.0246(7) Å for C13.

The Cr–C bond distances are 1.859(2)–1.883(2) Å for **1**. The two Cr–C bonds mutually *trans* are longer (weaker) than those *trans* to Cr–P bonds (Table 2). This result reflects the difference in the strength of the metal-to-ligand π -bonding

[21]. The aromatic rings in **1** as expected have usual bond lengths and angles.

4. Conclusion

In conclusion, we have shown the synthesis and molecular structure of *cis*-chelated tetracarbonylchromium(0) complex **1**. The Cr-atom has a distorted octahedral arrangement with four CO ligands and two P-centers. The two Cr–C bonds mutually *trans* are longer (weaker) than those *trans* to Cr–P bonds due to the various strengths of the metal-to-ligand π -bonding.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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