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 with (C$_5$H$_5$NH)$_2$Cr(CO)$_5$ afforded cis-[Cr(CO)$_5$(C$_5$H$_5$N-N-P(PPh$_2$)$_2$)]. This complex was crystallized in the monoclinic space group $P2_1/n$. 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 two P-atoms and C-atom attached to it. The four-membered metallacyclic ring P$_2$CrN 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], herein we report the synthesis and crystal structure of cis-[Cr(CO)$_5$(C$_5$H$_5$N-N-P(PPh$_2$)$_2$)] (I).

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)$_5$ were used as purchased. C$_{10}$H$_7$-N(PPh$_2$)$_2$ [1] and (C$_5$H$_5$NH)$_2$Cr(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$^\circ$C on a Bruker-Avance-DRX-400 MHz NMR spectrometer operating at 400.17 (H) and 100.63 (C) 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) (I). A solution of $N,N$-bis(diphenylphosphanyl)naphthylamine (0.26 g, 0.51 mmol) and (C$_5$H$_5$NH)$_2$Cr(CO)$_5$ (0.17 g, 0.51 mmol) in 20 mL of CH$_2$Cl$_2$ 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$^\circ$C gave 3 as yellow crystals in 85% yield. Mp 180–183$^\circ$C. $^1$H NMR (CDCl$_3$, $\delta$/ppm): 6.40–7.78 (m, 27 H, C$_6$H$_5$). $^{13}$C NMR (CDCl$_3$, $\delta$/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 (C$_{10}$H$_7$ and 4C$_6$H$_5$), 221.2 (C $\equiv$ O$_{eq}$), 228.2 (C $\equiv$ O$_{ax}$). $^{31}$P NMR (CDCl$_3$, $\delta$/ppm): 117.41 (s, 2P). IR (selected bands, KBr, cm$^{-1}$): $\delta$ = 1886 (s, br), 1920 (s), 2008 (s) (C $\equiv$ 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 I.

| Property     | Value       |
|--------------|-------------|
| Formula      | C₃₈H₂₇CrNO₄P₂ |
| M_r         | 675.55      |
| Temp [K]    | 150(2)      |
| Crystal system | Monoclinic |
| Space group  | P2₁/n       |
| a [Å]       | 12.209(5)   |
| b [Å]       | 20.003(5)   |
| c [Å]       | 13.954(5)   |
| α [°]       | 90          |
| β [°]       | 101.085(5)  |
| γ [°]       | 90          |
| V [Å³]      | 3344(2)     |
| Z           | 4           |
| μ [mm⁻¹]    | 1.4806      |
| ρcalcd [Mg m⁻³] | 1.342      |
| F(000)      | 1392        |
| No. of rflns | 6488        |
| R int       | 0.0223      |
| No. of param | 415         |
| wR2 (all data) | 0.0869    |

Table 2: Selected bond lengths (Å) and bond angles (deg.) for I.

| Bond          | Length [Å] | Angle [°] |
|---------------|------------|-----------|
| Cr1–C11      | 1.883(2)   | 86.31(7)  |
| Cr1–C12      | 1.859(2)   | 97.99(6)  |
| Cr1–C13      | 1.865(2)   | 94.26(5)  |
| Cr1–C14      | 1.881(2)   | 94.19(5)  |
| Cr1–P1       | 2.347(1)   | 97.99(7)  |
| Cr1–P2       | 2.347(1)   | 97.99(7)  |
| Cr1–N1       | 1.719(1)   | 90.89(6)  |
| Cr1–P1–N1    | 1.722(1)   | 90.89(6)  |
| Cr1–P1–C15   | 1.829(2)   | 68.74(3)  |
| P1–C14–P2    | 1.819(2)   | 82.97(6)  |
| P2–C11–C15   | 1.830(2)   | 94.26(5)  |
| Ni–C1–N1     | 1.443(2)   | 94.19(5)  |
| C11–O1–P1–C15| 1.136(2)   | 105.49(7) |
| C12–O2–P1–C21| 1.147(2)   | 109.46(8) |
| C13–O3–N1–P2–C27| 1.140(2) | 106.55(8) |
| C14–O4–N1–P2–C33| 1.146(2) | 109.00(7) |
| C12–P1–C14–P2–C33| 1.146(3) | 109.97(8) |
| C12–P1–C14–P2–C33| 93.02(9)  | 104.42(8) |
| C12–C11–P1–C21| 86.43(9)  | 110.70(7) |

3. Results and Discussion

3.1. Synthesis. Complex I was previously prepared by the reaction of Cr(CO)₆ with C₆H₆-N-(PPh₃)₂ in refluxing toluene for 36 hours [1]. Here, an alternative synthetic methodology was devised using (C₅H₅NH)Cr(CO)₅ instead of Cr(CO)₆ in refluxing CH₂Cl₂ to avoid prolonged refluxing time and further purification of the desired product. This methodology gave I 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 I were obtained as described in the Experimental Section. I crystallizes in the monoclinic space group P2₁/n. Selected interatomic distances and angles are collected in Table 2. The molecular structure is depicted in Figure 1.

The crystal structure of I 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(diphenylphosphinyl)naphthylamine ligand to act as bidentate P₂P'-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)°, with a smaller P–Cr–P–P bite angle [68.74(3)°] and larger P–N–P bond angle [100.70(7)°] (Table 2). The nitrogen atom is displaced out of the plane (Crl, 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 P₂P'-chelating bis(phosphino)amine
ligand, namely, cis-[Cr(CO)$_4$\{((o-MeOC$_6$H$_4$)$_2$P)$_2$NCH$_3$\}] (2) [17], cis-[Cr(CO)$_4$\{Ph$_2$P$_2$NPr\}] (3) [18], and cis-[Cr(CO)$_4$\{(Ph$_2$P)$_2$NH\}] (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)$^\circ$, 3 [67.82(4)$^\circ$, and 4 [68.58(2)$^\circ$. The P–N–P bond angle in 1 is smaller than those in 2 [101.24(7)$^\circ$ and 4 [103.24(9)$^\circ$ and larger than those in 3 [99.86(11)$^\circ$.

The P–N–P [100.70(7)$^\circ$] 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-napthyl skeleton in 1 is almost planar and virtually perpendicular to the P–Cr–P–N plan. 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$^\circ$ (Table 2). The P–Cr–C trans angles of 1 [166.57(7) and 168.99(6)$^\circ$] differ significantly from 180$^\circ$.

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 $\pi$-bonding. Consistent with this, the nitrogen atom is planar as evidenced by the sum of angles about nitrogen being 359.91(9)$^\circ$ 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 $\pi$-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 $\pi$-bonding
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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