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COMMUNICATION

SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF *CIS*-$(CO)_4Cr[(Me_3SiN)C(Ph)(NHPPh_2)]$

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Abstract—The interaction of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ with one equivalent of $C_7H_8Cr(CO)_4$ in diethyl ether gave *cis*-$(CO)_4Cr[(Me_3SiN)C(Ph)(NHPPh_2)]$ in good yield. The compound has been fully characterized by analytical, spectroscopic and X-ray diffraction methods. The NH proton of the bidentate iminophosphine ligand undergoes facile deuterium exchange with D_2O at ambient temperature. A 1,3-silyl shift mechanism has been proposed for the formation of the product.

Phosphorus–nitrogen compounds are π-electron-rich compounds and are potential precursors for inorganic polymers with unusual properties.[1,2] This has led to a considerable interest in the syntheses of phosphorus–nitrogen compounds[3] and the coordination chemistry of these compounds toward transition metals.[4] The coordination chemistry of $(Ph_2PN)\ [N(SiMe_3)_2]\ CC_6H_4C\ [N(SiMe_3)_2]\ (NPPh_2)$ has been briefly examined recently.[5] In this communication, we report the result of the interaction of $C_7H_8Cr(CO)_4$ with $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$.

When $C_7H_8Cr(CO)_4$ was allowed to react with one equivalent of $(Ph_2PN)C(Ph)[N(SiMe_3)_2]$ in diethyl ether for 2 days at room temperature, work-up gave yellow crystals of stoichiometry $(CO)_4Cr(C_{22}H_{25}N_2SiP)$,† **I**, in good yield (75%) after recrystallization from a diethyl ether/hexane mixture. The IR spectrum (KBr) of **I**, in the carbonyl region, exhibited four absorptions at 2004s, 1900vs, 1880vs and 1822vs cm^{-1}. The absorption pattern is indicative of a *cis*-configuration for the four terminal carbonyl groups. The IR spectrum also exhibited a strong absorption at 3352 cm^{-1} indicating the presence of a NH group. The $^{31}P\{^1H\}$ NMR spectrum of **I** in C_6D_6 exhibited a singlet at δ112.0 ppm for the PPh_2 group. The positive increase in the chemical shift for the PPh_2 group

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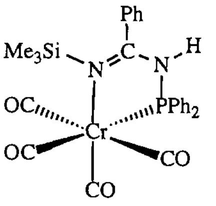
† $(CO)_4Cr(C_{22}H_{25}N_2SiP)$: yellow crystals, m.p. 173–175°C (dec.). Found: C, 57.9; H, 4.7; N, 5.1. Calc. for $C_{26}H_{25}N_2O_4SiPCr$: C, 57.8; H, 4.7; N, 5.2%. IR (cm^{-1}, in KBr): 3352s, 3056w, 2956w, 2004s, 1900vs, 1880vs, 1822vs, 1606m, 1584s, 1484w, 1436m, 1408s, 1328w, 1252m, 1184w, 1156w, 1098m, 1024w, 998w, 932m, 824s, 760m, 696s, 682s, 644s, 560m, 492m. $^{31}P\{^1H\}$ NMR (C_6D_6): δ112.0 (s) ppm. ^1H NMR (C_6D_6): phenyl protons, δ7.46 (4H, m), 7.02 (7H, m), 6.86 (2H, t, $J = 7.5$ Hz), 6.59 (2H, d, $J = 7.5$ Hz) ppm; NH proton, δ5.90 (1H, d, $J_{P-NH} = 6.3$ Hz) ppm; Me_3Si protons, δ0.17 (9H, s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): carbonyl carbons, δ228.8 (d, $J_{P-C} = 13.4$ Hz), 227.7 (d, $J_{P—C} = 2.5$ Hz), and 220.0 (d, $J_{P-C} = 14.7$ Hz) ppm; C=N carbon, δ169.7 (d, $J_{P—NC} = 19.6$ Hz) ppm; phenyl carbons of C—Ph, δ130.6, 130.0, 128.9, 126.9 ppm; phenyl carbons of PPh_2, 137.7 (d, $J_{P—C} = 39.1$ Hz), 137.6 (d, $J_{P—C} = 4.8$ Hz), 130.8 (d, $J_{P—C} = 13.4$ Hz), 128.8 (d, $J_{P—C} = 2.4$ Hz) ppm; Me_3Si carbons, 3.6 (s) ppm.

(from δ37.4 to 112.0 ppm) is characteristic of chelate ring formation.[6] In addition to the resonances expected for the phenyl protons and carbons, the ^{1}H NMR spectrum of **I** exhibited a doublet and a singlet of relative intensity 1 : 9 at δ5.90 (J_{P-NH} = 6.3 Hz) and 0.17 ppm for the NH and SiMe$_3$ protons, respectively; and the ^{13}C NMR spectrum exhibited three doublets at δ228.8 (J_{P-C} = 13.4 Hz), 227.7 (J_{P-C} = 2.5 Hz) and 220.0 (J_{P-C} = 14.7 Hz) ppm for the terminal carbonyl carbons, a doublet at δ169.7 (J_{P-NC} = 19.6 Hz) ppm for the C=N carbon, and a singlet at δ3.6 ppm for the trimethylsilyl carbons. Based on the above spectroscopic data, the following structure can be assigned to **I**.



I

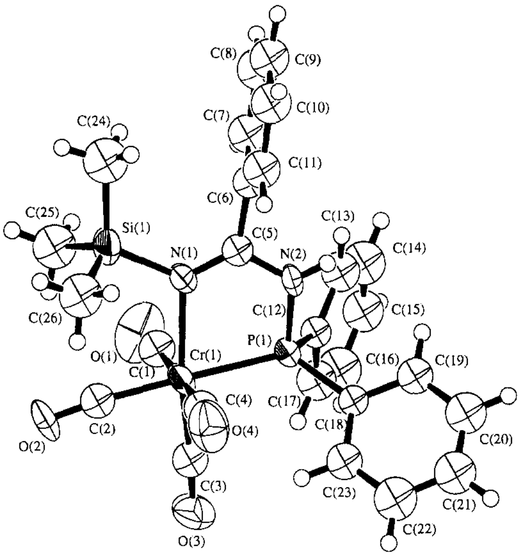


Fig. 1. A perspective view of the molecular structure of *cis*-(CO)$_4$Cr[(Me$_3$SiN)C(Ph)(NHPPh$_2$)]. Selected bond lengths (Å) and bond angles (°) : Cr(1)—P(1), 2.329(2); Cr(1)—N(1), 2.216(6); Cr(1)—C(1), 1.86(1); Cr(1)—C(2), 1.841(10); Cr(1)—C(3), 1.82(1); Cr(1)—C(4), 1.88(1); P(1)—N(2), 1.706(7); N(2)—C(5), 1.359(10); N(1)—C(5), 1.293(10); P(1)—Cr(1)—N(1), 79.7(2); P(1)—Cr(1)—C(1), 92.4(3); P(1)—Cr(1)—C(2), 179.4(3); P(1)—Cr(1)—C(3), 93.8(3); P(1)—Cr(1)—C(4), 90.8(3); Cr(1)—N(1)—C(5), 116.8(6); N(1)—C(5)—N(2), 122.3(8); C(5)—N(2)—P(1), 119.0(5).

The structure of **I** was confirmed by an X-ray diffraction study.† A perspective drawing and selected bond lengths and bond angles of **I** are shown in Fig. 1. The solid-state structure of **I** is consistent with its spectroscopic data. The (Me$_3$SiN)C(Ph)(NHPPh$_2$) acts as a chelating ligand with the imino group N(1) and the phosphino group P(1) coordinated to the Cr(CO)$_4$ moiety forming a five-membered ring. The geometry of Cr is approximately octahedral with the four terminal carbonyl ligands adopting a *cis*-configuration. The Cr—C distances of the Cr(CO)$_4$ moiety show the expected pattern for a *cis*-(CO)$_4$CrL$_2$ complex with L being a poorer π-acid than CO. The Cr—C distances of the two mutually *trans*-carbonyls are 1.86(1) and 1.88(1) Å for Cr(1)—C(1) and Cr(1)—C(4), respectively, and are slightly longer than the Cr—C distances of 1.82(1) and 1.84(1) Å for the carbonyls *trans* to the imino N(1) and phosphino P(1) groups, respectively.

Within the bidentate iminophosphine ligand, the P(1)—N(2) bond length of 1.706(7) Å is in the normal range for a phosphorus–nitrogen single bond. The C(5)—N(1) and C(5)—N(2) distances of 1.293(10) and 1.359(10) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.26 Å) bonds indicating some delocalization about the N—C—N framework. The delocalization is also reflected in the P(1)—N(2)—C(5) bond angle of 119.0(5)° which deviates significantly from the expected for a tetrahedral sp^3 nitrogen atom and is closer to a sp^2 nitrogen atom. Similar observation has been reported for related palladium[5] and rhodium complexes.[7]

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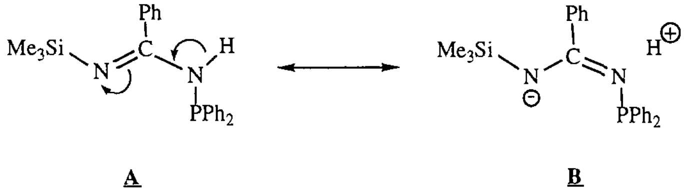
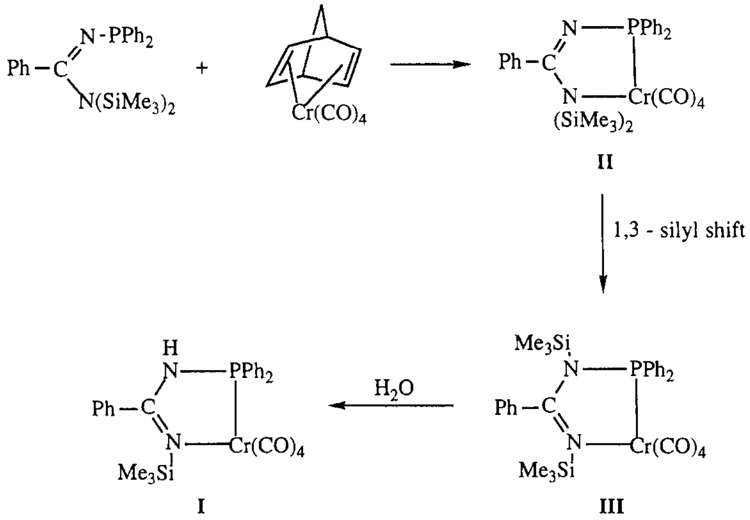
† Crystal data: C$_{26}$H$_{25}$N$_2$O$_4$SiPCr, Fw = 540.54, monoclinic, $P2_1/n$ (No. 14, non-standard setting of $P2_1/c$), a = 8.995(1), b = 20.862(4), c = 15.042(5) Å, β = 101.85(2)°, V = 2763(1) Å^3, Z = 4, F(000) = 1120, D_c = 1.300 g cm^{-3}, μ = 5.48 cm^{-1}. Crystal dimensions: 0.21 × 0.24 × 0.33 mm. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω-2θ scans (2θ max = 50°, 3821 unique reflections) at 293 K. The structure was solved by a combination of Patterson and difference Fourier techniques and refined by full-matrix least-squares analysis to give R = 0.058, Rw = 0.068 for 1749 independent observed reflections [$I > 3\sigma(I)$]. Cr, P, Si, O and N atoms were refined anisotropically and the rest of the atoms were refined isotropically. Hydrogen atoms were placed in their idealized positions and included in the calculations but not refined. All calculation were performed on a Silicon-Graphics computer using the program package TeXan[8] from MSC.



Scheme 1.



Scheme 2. Possible mechanism for the formation of **I**.

There are two possible resonance structures for the iminophosphine ligand. These are shown in Scheme 1. The above structural data suggest that both resonance forms are important contributors to the structure of **I**. The contribution of the ionic resonance form **B** to the structure of **I** is further supported by the fact that the imino proton of **I** underwent facile deuterium exchange with D_2O at ambient temperature.

A possible mechanism for the formation of **I** is shown in Scheme 2. $C_7H_8Cr(CO)_4$ reacted with the ligand to produce intermediate **II**, which underwent rapid 1,3-silyl shift to give intermediate **III**. **III** then hydrolysed to produce the final product. Similar mechanism has been proposed for related complexes.[5,7]

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REFERENCES

1. H. W. Roesky and M. Lucke, *Angew. Chem., Int. Ed. Engl.* 1989, **28**, 493.
2. J. A. Dodge, I. Manners, H. R. Allcock, G. Renner and O. Nuyken, *J. Am. Chem. Soc.* 1990, **112**, 1268, and references cited therein.
3. V. Chandrasekhar, T. Chivers, S. S. Kumaravel, A. Meetsma and J. C. van de Grampel, *Inorg. Chem.* 1991, **30**, 3402, and references cited therein.
4. T. Chivers, K. McGregor and M. Parvez, *Inorg. Chem.* 1994, **33**, 2364 and references cited therein.
5. W.-K. Wong, T. Jiang, D. W. J. Kwong and W.-T. Wong, *Polyhedron* 1995, **14**, 1109.
6. K. R. Dixon, *Multinuclear NMR*, (Edited by J. Mason), Ch. 13. Plenium Press, New York (1987).
7. T. Chivers, K. McGregor and M. Parvez, *Inorg. Chem.* 1993, **32**, 5119.
8. TeXan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).