ELSEVIER

Journal of Organometallic Chemistry 631 (2001) 188–192

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Facile displacement of cyclohexadienide ligand from K[Cr(η^5-C_6H_7)$(CO)_3$] to give crystallographically characterized *trans*-[Cr$(CO)_4(PPh_3)_2$]

Jian Bao, Steven J. Geib [1], N. John Cooper *

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA

Received 31 October 2000; received in revised form 1 May 2001; accepted 2 May 2001

Abstract

Substitution of K[Cr(η^5-C_6H_7)$(CO)_3$] with triphenylphosphine resulted in cyclohexadienide loss and formation of an unexpected product, *trans*-[Cr$(CO)_4(PPh_3)_2$]. The structure of this complex was determined by single crystal X-ray diffraction. Crystals contain two conformational isomers, differing mainly in the orientation of PPh_3 ligands. © 2001 Published by Elsevier Science B.V.

Keywords: Cyclohexadienyl; Chromium; Triphenylphosphine; Carbonyl complexes; Ligand replacement

1. Introduction

Cyclohexadienyl complexes of Cr(0) are readily prepared by exo-addition of soft carbanionic nucleophiles to the aromatic ring in [Cr(η^6-C_6H_6)$(CO)_3$] (**1**) and its many substituted derivatives, and the potential of these species as intermediates in manipulations of the aromatic ring that can be of value in organic syntheses has been extensively explored [1].

Less attention has been paid to the inorganic chemistry of these systems, but our convenient access [2] to the parent cyclohexadienyl complex [Cr(η^5-C_6H_7)-$(CO)_3]^-$ (**2**$^-$) through protonation of the reductively activated η^4-benzene complex [Cr(η^4-C_6H_6)$(CO)_3]^{2-}$, recently led us to explore substitution reactions of K[Cr(η^5-C_6H_7)$(CO)_3$]. We now wish to report that this results in an unexpected displacement of the cyclohexadienide anion to provide access to the Cr(0) carbonyl phosphine complex *trans*-[Cr$(CO)_4(PPh_3)_2$] (**3**). The *trans* isomer of [Cr$(CO)_4(PPh_3)_2$] was first reported by Hieber and co-workers in 1959 [3a], and has long been recognized as the more stable one of the two possible isomers of [Cr$(CO)_4(PPh_3)_2$] [3b]; surprisingly, however, this archetypal disubstituted phosphine carbonyl complex has never been crystallographic characterized. Our procedure has provided access to crystalline samples of the *trans*-[Cr$(CO)_4(PPh_3)_2$] that has now allowed crystallographic characterization of this classic complex.

2. Results and discussion

Samples of K[Cr(η^5-C_6H_7)$(CO)_3$] (K**2**) were prepared by two equivalent KNap reduction of **1** in THF at -78°C followed by in situ protonation with H_2O. Substitution of the cyclohexadienyl complex K**2** with PPh_3 was carried out at room temperature by addition of 3 equivalents of PPh_3 as shown in Scheme 1.

Infrared spectroscopy showed the disappearance of the C≡O stretches of the starting complex and the appearance of a new band at 1880 cm^{-1} indicating the formation of a new carbonyl complex. After work-up as described in Section 4, the product was obtained as yellow cubic crystals. These were shown to be

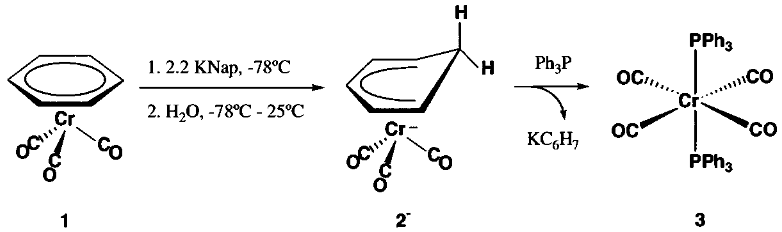
---

* Corresponding author. Fax: +1-412-624 6089.

E-mail address: cooper@pitt.edu (N.J. Cooper).

[1] Address: Crystallographic correspondence to their author.

0022-328X/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0022-328X(01)00929-9



Scheme 1.

$[Cr(CO)_4(PPh_3)_2]$ by IR, NMR and elemental analysis; the single band in the IR spectrum suggested that we had obtained **3** as the *trans* isomer.

Zero-valent complexes $[Cr(CO)_4(PR_3)_2]$ have been known since early work by Hieber, and have been subjected to electrochemical, photochemical, and spectroscopic investigations [4]. The structure of the analogous molybdenum complex [5] has been reported in both *cis* [5a] and *trans* [5b] configurations, but the only structural studies of bisphosphine chromium carbonyl phosphine complexes [6] are of *cis*-$[Cr(CO)_4(PH_3)_2]$ [6a] and $[Cr(CO)_4(Ph_2PCH_2)_2]$ [6b]. The PPh_3 complexes have a much more extensive chemistry than the PH_3 complexes, and it is of obvious value to determine structural parameters for **3**, particularly given recent theoretical interest in this molecule [7]. Our procedure provided ready access to crystallographic quality crystals of **3** and we determined the structure of the molecule as described in Section 4. Crystallographic data and structural parameters for **3** are summarized in Tables 1 and 2. The diffraction study confirmed that **3** had been formed in the *trans* form.

Crystals of **3** contain molecules in two conformational isomers, one of which has twofold symmetry and two symmetric triphenylphosphine ligands. The Cr atom of this conformer (Cr1′) is at a molecular center of inversion, while the other conformer has triphenylphosphine ligands with slightly different orientations of the phenyl groups (Fig. 1). The two conformers are present in a 1 to 2 ratio, with the asymmetric conformer as the major species. The unit cell contains three molecules with a crystallographic inversion center at the Cr1′ atom of the symmetric molecule.

The inversion center in the symmetric molecule renders the two phosphorus atoms directly *trans* to one another (P1′–Cr1′–P1′A = 180°). The metal center in this unit is close to an ideal octahedral geometry, with the P–Cr–C angles ranging from 88.1(1) to 91.1(1)°. The Cr–P bond length is 2.356(1) Å. Cr–P distances in all crystallographically characterized $[Cr(CO)_4(PR_3)_2]$ complexes are compared in Table 3.

In the asymmetric molecule the four carbonyl carbon atoms and the Cr have a rms average deviation of 0.039 Å from the least square plane, and the two Cr–P bond lengths differ significantly. One PPh_3 has a rotated phenyl ring (45°), and has a Cr–P bond at 2.371(1) Å as compared with 2.347(1) Å. The 0.024 Å difference between these values is more than 20σ, but their average value of 2.359 Å is close to the Cr–P distance in the symmetric molecule, suggesting that there is a soft potential energy surface for *trans*-$[Cr(CO)_4(PPh_3)_2]$ that allows marked changes in molecular parameters in response to crystal packing forces.

3. Conclusion

Reaction of the cyclohexadienyl complex $K[Cr(\eta^5\text{-}C_6H_7)(CO)_3]$ with excess Ph_3P does not result in the anticipated carbonyl substitution reaction but instead

Table 1
Crystal data and structure refinement for **3**

Empirical formula	$C_{40}H_{30}CrO_4P_2$
Formula weight	688.58
Temperature (K)	208(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	10.184(2)
b (Å)	10.621(2)
c (Å)	25.756(5)
α (°)	88.01(3)
β (°)	83.45(3)
γ (°)	65.35(3)
Volume (Å^3)	2515.2(9)
Z, Calculated density (Mg m^{-3})	3, 1.364
Absorption coefficient (mm^{-1})	0.478
$F(000)$	1068
Crystal size (mm)	$0.21 \times 0.24 \times 0.31$
θ range for data collection (°)	2.11–25.00
Limiting indices	$0 \leq h \leq 12$, $-12 \leq k \leq 12$, $-30 \leq l \leq 30$
Reflections collected/unique	9414/8865 [$R_{int} = 0.0222$]
Completeness to $\theta = 25.00$ (%)	99.9
Absorption correction	Psi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8865/0/637
Goodness-of-fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1043$
R indices (all data)	$R_1 = 0.0859$, $wR_2 = 0.1231$
Largest difference peak and hole (e Å^{-3})	0.487 and −0.235

Table 2
Selected bond lengths (Å) and angles (°) for symmetric [Cr(1′)] and asymmetric [Cr(1)] **3**

Cr1–C2	1.873(3)	Cr1′–C1′	1.884(3)
Cr1–C3	1.878(3)	Cr1′–C2′	1.885(3)
Cr1–C1	1.881(3)	Cr1′–P1′	2.3562(13)
Cr1–C4	1.896(3)	O1–C1	1.154(4)
Cr1–P2	2.3474(14)	O1′–C1′	1.149(4)
Cr1–P1	2.3714(14)	O2–C2	1.147(4)
C4–O4	1.143(4)	O2′–C2′	1.150(4)
O3–C3	1.152(4)		
C2–Cr1–C3	91.89(14)	C2′–Cr1′–P1′	90.82(10)
C2–Cr1–C1	83.79(15)	C1′–Cr1′–P1′	88.84(10)
C3–Cr1–C4	92.19(14)	C4–Cr1–P1	87.86(10)
C1–Cr1–C4	92.21(14)	P2–Cr1–P1	176.15(4)
C2–Cr1–P2	87.53(11)	C1′A–Cr1′–C2′	89.28(13)
C3–Cr1–P2	89.82(10)	C1′–Cr1′–C2′	90.72(13)
C1–Cr1–P2	91.32(10)	C3–Cr1–P1	88.93(10)
C4–Cr1–P2	88.55(10)	C1–Cr1–P1	90.20(10)
C2–Cr1–P1	96.15(11)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$.

in loss of a cyclohexadienide anion and, after carbonyl redistribution, formation of *trans*-[Cr(CO)$_4$(PPh$_3$)$_2$]. This contrasts sharply with the corresponding chemistry of neutral cyclopentadienyl and cyclohexadienyl complexes [8] like [Mn(η^5-C$_5$H$_5$)(CO)$_3$] [8a,b] and [Mn(η^5-C$_6$H$_7$)(CO)$_3$] [8c]. We attribute this difference primarily to the fact that loss of a cyclohexadienide group from [Cr((η^5-C$_6$H$_7$)(CO)$_3$]$^-$ does not involve the charge separation that would be inherent in analogous reactions of [Mn(η^5-C$_5$H$_5$)(CO)$_3$] or [Mn(η^5-C$_6$H$_7$)(CO)$_3$]. We note also that the higher electron density on the anionic Cr center in **2**$^-$ does imply that increased back donation to the CO ligands in **2**$^-$ would bind them more tightly than in complexes of Mn(1) like [Mn(η^5-C$_5$H$_5$)(CO)$_3$] and [Mn(η^5-C$_6$H$_7$)(CO)$_3$], and it is well established in phosphine carbonyl complexes that increased back donation decreases the lability of the carbonyl ligands.

4. Experimental

4.1. General procedures

All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen by means of standard Schlenk techniques or a Vacuum Atmospheres drybox as described in recent publications from this group [9].

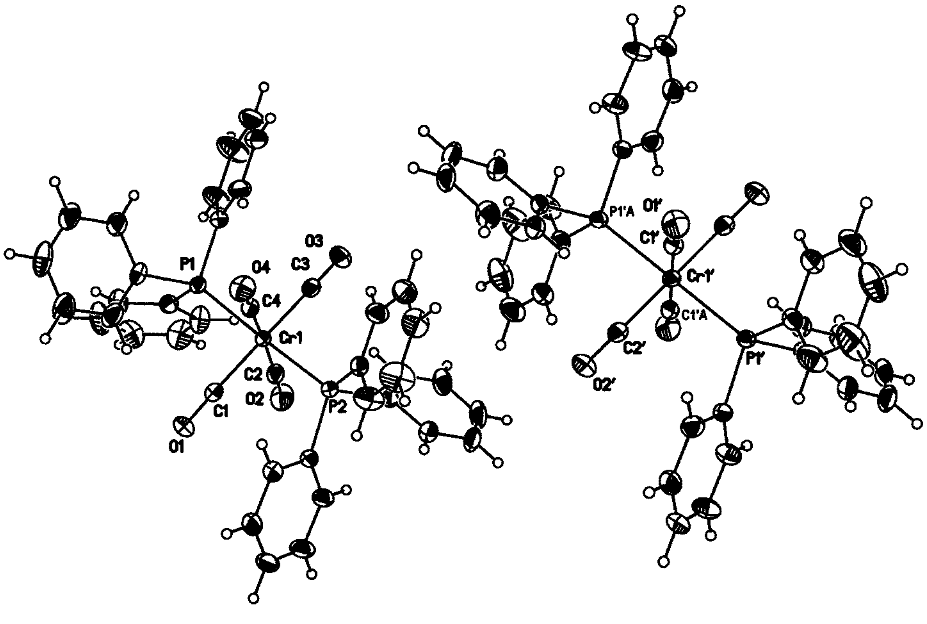


Fig. 1. ORTEP drawing of [Cr(CO)$_4$(PPh$_3$)$_2$] (35% probability ellipsoids).

Table 3
Comparison of the Cr–P bond lengths in octahedral [Cr(CO)$_4$(PR$_3$)$_2$] complexes {[M] = Cr(CO)$_4$}

Distance (Å)	[M] [Ph$_2$P(CH$_2$)$_2$]$_2$	*Cis*-[M](PH$_3$)$_2$	*Trans*-[M](POPh$_3$)$_2$	Symmetric **3**	Asymmetric **3**
Cr–P	2.360	2.349(4)	2.252(1)	2.356(1)	2.347(1), 2.371(1)
P–Cr–P			4.504(2)	4.712(2)	4.718(2)
Reference	[6b]	[6a]	[11]	This work	

All solvents were freshly distilled under nitrogen before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were pre-dried over sodium ribbon. THF was distilled from potassium, and Et_2O was distilled from sodium–benzophenone ketyl. *n*-Pentane was stirred over concentrated H_2SO_4 for more than 24 h, neutralized with K_2CO_3, and distilled from CaH_2. Deuterated NMR solvents were purchased from Cambridge Isotope Labs and used as received. Chromium carbonyl $[Cr(CO)_6]$ was purchased from Strem Chemicals and used as received.

Potassium naphthalenide $[K(C_{10}H_8)]$ was prepared by dissolution of freshly cut potassium metal (Aldrich) in a solution (0.2 M) of naphthalene (1.0 equivalent) in THF. The mixture was stirred for 8 h at room temperature, and potassium naphthalenide solutions were stored at -70°C.

Samples of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) were prepared from $[Cr(CO)_6]$ in 70% yield by a local modification of the literature procedure [10].

Infrared spectra were recorded on a Perkin–Elmer model 783 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 Hz. ^{13}C-NMR spectra were recorded on a Bruker AC 300 at 75 MHz. Microanalyses were performed by Atlantic Microlab, Norcross, GA.

Crystals for X-ray diffraction studies were coated with fluorolube then mounted on a glass fiber and coated with epoxy. X-ray data were collected on a Siemens P3 diffractometer using graphite monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å). Data processing and graphics were done with the Siemens SHELXTL package program. All non-hydrogen atoms were located and refined anisotropically. All hydrogen atoms in $[Cr(CO)_4(PPh_3)_2]$ were located and refined isotropically.

4.2. Reaction of $K[Cr(\eta^5\text{-}C_6H_7)(CO)_3]$ with Ph_3P

A 0.2 M solution of freshly prepared KNap in THF (12.8 ml, 2.57 mmol, 2.2 equivalents) was added by syringe to a vigorously stirred solution of **1** (0.25 g, 1.17 mmol) in 50 ml THF at -78°C. Addition of 1 equivalent of H_2O (21 µl, 1.17 mmol) gave the adduct anion $[Cr(\eta^5\text{-}C_6H_7)(CO)_3]^-$ ($\mathbf{2}^-$) instantly. The reaction was monitored by infrared monitoring of the fingerprint ν_{CO} absorptions of the complexes. The reaction was warmed to room temperature before Ph_3P (0.92 g, 3.51 mmol, 3 equivalents) was added and then stirred overnight. The solvent was then removed under vacuum and the residue was washed with pentane (30 ml × 3) and then Et_2O (30 ml × 3). This procedure left *trans*-$[Cr(CO)_4(PPh_3)_2]$ (**3**) as the reaction product (0.31 g, 0.45 mmol, yield 38% relative to the metal). Anal. Calc. for $C_{40}H_{30}CrO_4P_2$: C, 69.77; H, 4.39. Found: C, 69.96; H, 4.33%. The IR spectrum of the product is comparable to that in the literature [3]. IR ($\nu_{C\equiv O}$, Nujol mull) 1980 (vs) cm^{-1}. ^{1}H-NMR (300 MHz, CD_2Cl_2, rt) δ 7.57 (m, 2H), 7.39 (m, 3H). ^{31}P-NMR (75 MHz, CD_2Cl_2, rt) δ 74.7. Crystallographic quality crystals were formed by slowly adding a layer of Et_2O (3 volumes) onto a saturated THF solution of **3**. Crystals were formed in ca. 1 week, and collected in 30% yield after removal of the solution through a cannula.

5. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 163156. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by the NSF through grant number CHE 9632202 to N.J.C.

References

[1] (a) For reviews, see: M.F. Semmelhack, in: B. Trost, L. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon, Oxford, 1992, p. 521 and references cited therein;
(b) M.F. Semmelhack, H. Schmalz, Tetrahedron Lett. 37 (1996) 3089;
(c) F. Rose-Munch, V. Gagliardini, C. Renard, E. Rose, Coord. Chem. Rev. 180 (1998) 249;
(d) K. Schellhaas, H.G. Schmalz, J.W. Bats, Chem-A Euro. J. 4 (1998) 57;
(e) L.S. Hegedus, Coord. Chem. Rev. 168 (1998) 49;
(f) F. Rose-Munch, E. Rose, Curr. Org. Chem. 3 (1999) 445.

[2] (a) V.S. Leong, N.J. Cooper, J. Am. Chem. Soc. 110 (1988) 2644 and references cited therein;
(b) J.A. Corella, N.J. Cooper, J. Am. Chem. Soc. 112 (1990) 2832.

[3] (a) W. Hieber, J. Peterhans, Z. Naturforsch. Teil B 14 (1959) 462;
(b) A. Magee, C.N. Matthews, T.S. Wang, J.H. Wotiz, J. Am. Chem. Soc. 83 (1961) 3200.

[4] (a) R.N. Bagchi, A.M. Bond, R. Colton, D.L. Luscombe, J.E. Moir, J.E. Kevekordes, Organometallics 3 (1984) 4;
(b) S.W. Kirtley, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982, p. 783.

[5] (a) F.A. Cotton, D.J. Darensbourg, S. Klein, B.W.S. Kolthammer, Inorg. Chem. 21 (1982) 294;
(b) G. Hogarth, T. Norman, Inorg. Chim. Acta 254 (1997) 167.

[6] (a) L.S. Guggenberger, U. Klabunde, R.A. Schunn, Inorg. Chem. 12 (1973) 1143;

(b) M.J. Bennett, F.A. Cotton, M.D. LaPrade, Acta Crystallogr. Sect. B 27 (1971) 1899.

[7] D.A. Cummings, J. McMaster, A.L. Rieger, P.H. Rieger, Organometallics 16 (1997) 4362.

[8] (a) R.J. Angelici, E. Efraty, J. Organomet. Chem. 23 (1970) 527; (b) M.E. Rerek, L.-N. Ji, F. Basolo, J. Chem. Soc. Chem. Commun. (1983) 1208; (c) J.B. Sheridon, R.S. Padda, K. Chaffee, C.J. Wang, Y.Z. Huang, R. Lalancette, J. Chem. Soc. Dalton Trans. (1992) 1539.

[9] J.M. Veauthier, A. Chow, G. Fraenkel, S.J. Geib, N.J. Cooper, Organometallics 19 (2000) 661.

[10] C.A.L. Mahaffy, P.L. Paulson, Inorg. Synth. 19 (1979) 154.

[11] H.S. Preston, J.M. Stewart, S.O. Grim, Inorg. Chem. 11 (1972) 161.