

Acknowledgment. B.V.P. thanks the Council of Scientific and Industrial Research, New Delhi, for financial support. The computations are carried at National Informatic Centre, Hyderabad.

Appendix

The important geometric parameters used for compounds **3a**, **3b**, **8a**, **8b**, and **XXI** are given in Table II. The Walsh diagrams (Figure 5) are constructed by varying θ from 105 to 65°. As a function of θ , the R group on the carbynyl carbon is tilted away from the M(1)-C-M(2) plane and away from M(1) so that carbyne in the compounds at a smaller dihedral angle becomes a μ_3 bridge. The position of the bridging hydrogen is varied as a

function of θ . M(2)-C-M(3) vs M(2)-H-M(3) is maintained at 175°. The coordination of the carbonyls does not show any major change in II^{3e} and XVII.¹⁶ This prompted us to keep the coordination of carbonyls around the metals in the construction of the Walsh diagrams constant. Arbitrary variation of the CO ligands in such bulky molecules is not advisable because of steric reasons. The atomic parameters used for the extended Huckel calculations are taken from the literature, which suits best for the trimetallic clusters.^{34,29} The weighted H_{ij} formula is used. Distances are in angstrom units, and angles are in degrees.

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Complexes with Unbridged Dative Bonds between Osmium and a Group 6 Element. Structures of $(OC)_{5-x}(Bu^tNC)_x OsCr(CO)_5$ ($x = 1, 2$)

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Received August 23, 1990

The isocyanide derivatives $Os(CO)_{5-x}(Bu^tNC)_x$ ($x = 1, 2$) have been prepared from the reaction of $Os(CO)_5$ (or, for $x = 1$, $Os(CO)_4(\eta^2\text{-cyclooctene})$) and Bu^tNC . Reaction of these derivatives with $M(CO)_5(THF)$ ($M = Cr, Mo, W$) in hexane yields $(OC)_{5-x}(Bu^tNC)_x OsM(CO)_5$. The structures of $(OC)_4(Bu^tNC)OsCr(CO)_5$ (**1-Cr**) and $[cis\text{-}dieq\text{-}(OC)_3(Bu^tNC)_2Os]Cr(CO)_5$ (**2b-Cr**) have been determined by X-ray crystallography: compound **1-Cr** crystallizes in the space group $Pnam$ with $a = 20.272$ (4) Å, $b = 9.648$ (1) Å, $c = 9.843$ (2) Å, $Z = 4$, $R = 0.027$, and $R_w = 0.027$ for 1306 reflections ($I \geq 2.5\sigma(I)$); compound **2b-Cr** crystallizes in the space group $P2_1/n$ with $a = 9.129$ (1) Å, $b = 12.258$ (1) Å, $c = 20.863$ (3) Å, $\beta = 90.32$ (1)°, $Z = 4$, $R = 0.026$, and $R_w = 0.022$ for 2505 reflections ($I \geq 2.5\sigma(I)$). In both **1-Cr** and **2b-Cr** the 18-electron moiety $Os(CO)_{5-x}(CNBu^t)_x$ acts as a 2-electron donor ligand to the chromium atom in the $Cr(CO)_5$ unit via an unbridged, dative metal-metal bond (the Os-Cr distance is 2.966 (2) Å in **1-Cr** and 2.969 (2) Å in **2b-Cr**); the isocyanide ligands are in cis positions to the metal-metal bonds. The spectroscopic data for the $(OC)_4(Bu^tNC)OsM(CO)_5$ complexes indicate that the solid-state structure found for **1-Cr** is also adopted by these complexes in solution. There is no evidence for the isomer with the non-carbonyl ligand trans to the Os-M bond. This is in contrast to the $(R_3P)(OC)_4OsM(CO)_5$ complexes where this is the major, or only, isomer present in solution. The spectroscopic properties of the kinetically preferred products from the reaction of $Os(CO)_3(CNBU^t)_2$ with $M(CO)_5(THF)$ indicate the isocyanide ligands occupy equatorial sites on osmium that are mutually trans (i.e., $[trans\text{-}dieq\text{-}(OC)_3(Bu^tNC)_2Os]M(CO)_5$). When these complexes are stirred in CH_2Cl_2 solution at room temperature, they isomerize (over 2-10 days) to give an equilibrium mixture more concentrated in a second isomer. Spectroscopic data of pure samples of the second isomer indicate the Bu^tNC ligands are in equatorial positions on the osmium atom that are mutually cis (as indicated above, this was confirmed by X-ray crystallography for the chromium compound). Once again, there was no evidence for the isomer with an isocyanide ligand trans to the metal-metal bond.

Introduction

Work from this laboratory over the past 7 years has demonstrated that neutral, 18-electron metal carbonyl compounds can act as ligands. Some examples of complexes with this type of ligand are $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$,¹ $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$,² and $(Me_3P)(OC)_4OsRe(CO)_4(Br)$.³ The metal-metal bonds in these complexes are donor-acceptor (dative) bonds, and as shown by X-ray crystallography, they are unbridged.

In a recent paper we described the preparation of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ ($M = Cr, Mo, W$).⁴ The X-ray crystal structures of $(Me_3P)(OC)_4OsCr(CO)_5$ and its tungsten analogue revealed that the metal-metal bond is also unbridged with the phosphine ligand trans to the metal-metal bond. Carbon-13 NMR spectroscopy demonstrated that the isomer with the PR_3 ligand trans to the Os-M bond was also the major isomer present for these complexes in solution. For the complexes that had phosphorus ligands with a small cone angle, there were, however, significant amounts of the isomer with the PR_3 ligand cis to the Os-M bond present.⁴

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Table I. Analytical and Mass Spectral Data for New Compounds

	anal.						MS ^a
	calcd			found			
	C	H	N	C	H	N	
Os(CO) ₄ (CNBu ^t)	28.05	2.35	3.63	28.25	2.54	3.70	387
Os(CO) ₃ (CNBu ^t) ₂	35.45	4.12	6.36	35.65	4.08	6.29	442
(OC) ₄ (Bu ^t NC)OsCr(CO) ₅ (1-Cr)	29.12	1.57	2.42	29.35	1.69	2.50	579
(OC) ₄ (Bu ^t NC)OsMo(CO) ₅ (1-Mo)	27.06	1.46	2.25	27.25	1.48	2.05	623
(OC) ₄ (Bu ^t NC)OsW(CO) ₅ (1-W)	23.71	1.28	1.97	23.66	1.36	2.09	709
(OC) ₃ (Bu ^t NC) ₂ OsCr(CO) ₅ (2a-Cr)	34.18	2.87	4.43	34.56	2.97	4.18	634
(OC) ₃ (Bu ^t NC) ₂ OsMo(CO) ₅ (2b-Cr)	34.18	2.87	4.43	34.34	2.78	4.27	634
(OC) ₃ (Bu ^t NC) ₂ OsMo(CO) ₅ (2a-Mo)	31.96	2.68	4.14	31.76	2.67	3.93	678
(OC) ₃ (Bu ^t NC) ₂ OsMo(CO) ₅ (2b-Mo)	31.96	2.68	4.14	31.97	2.62	4.30	678
(OC) ₃ (Bu ^t NC) ₂ OsW(CO) ₅ (2a-W)	28.28	2.37	3.66	28.48	2.46	3.69	764
(OC) ₃ (Bu ^t NC) ₂ OsW(CO) ₅ (2b-W)	28.28	2.37	3.66	28.14	2.32	3.67	764

^a M⁺ ion.Table II. Infrared Data for New Compounds^a

	solvent ^b	ν(CN), cm ⁻¹		ν(CO), cm ⁻¹	
		ν(CN)	ν(CN)	ν(CO)	ν(CO)
Os(CO) ₄ (L)	hex	2191 (w)		2061 (s), 1996 (m), 1960 (vs)	
Os(CO) ₃ (L) ₂	hex	2136 (m)		1925 (vs)	
(OC) ₄ (L)OsCr(CO) ₅ (1-Cr)	hex	2206 (w)		2099 (m), 2040 (m), 2031 (vs), 2021 (vs), 1961 (w), 1921 (vs), 1914 (vs)	
(OC) ₄ (L)OsMo(CO) ₅ (1-Mo)	dich	2214 (w)		2102 (m), 2030 (vs), 1915 (vs)	
	hex	2205 (w)		2095 (m), 2048 (m), 2033 (m), 2019 (s), 2014 (s), 1973 (w), 1933 (vs), 1925 (s), 1914 (s)	
(OC) ₄ (L)OsW(CO) ₅ (1-W)	dich	2211 (m)		2097 (m), 2047 (s), 2013 (s), 1926 (vs), 1888 (m)	
	hex	2207 (w)		2099 (m), 2046 (m), 2039 (m), 2022 (s), 1963 (vw), 1922 (vs), 1915 (s), 1909 (sh)	
(OC) ₃ (L) ₂ OsCr(CO) ₅ (2a-Cr) ^c	dich	2214 (m)		2102 (m), 2044 (s), 2022 (s), 1915 (vs), 1884 (sh)	
	hex	2174 (m)		2060 (vw), 2014 (s), 1995 (s), 1909 (s), 1902 (vs)	
	dich	2181 (s)		2062 (vw), 2012 (vs), 1993 (s), 1904 (vs), 1870 (sh)	
(OC) ₃ (L) ₂ OsCr(CO) ₅ (2b-Cr)	dich	2208 (m), 2184 (m)		2061 (s), 2012 (vs), 1994 (sh), 1942 (vw), 1899 (vs), 1867 (sh)	
(OC) ₃ (L) ₂ OsMo(CO) ₅ (2a-Mo) ^c	hex	2170 (m)		2059 (w), 2026 (m), 1987 (s), 1921 (vs), 1913 (s), 1902 (s)	
	dich	2176 (s)		2058 (m), 2026 (s), 1984 (s), 1915 (vs), 1872 (m)	
(OC) ₃ (L) ₂ OsMo(CO) ₅ (2b-Mo)	dich	2204 (m), 2177 (m)		2058 (s), 2027 (s), 1994 (s), 1914 (vs), 1871 (m)	
(OC) ₃ (L) ₂ OsW(CO) ₅ (2a-W) ^c	hex	2173 (m)		2062 (vw), 2027 (m), 1995 (s), 1910 (vs), 1903 (s), 1899 (sh)	
	dich	2180 (m)		2062 (w), 2027 (m), 1989 (s), 1908 (vs), 1866 (m)	
(OC) ₃ (L) ₂ OsW(CO) ₅ (2b-W)	dich	2207 (m), 2182 (m)		2062 (s), 2027 (s), 2003 (s), 1951 (vw), 1904 (vs), 1865 (m)	

^a L = Bu^tNC. ^b Key: hex = hexane; dich = CH₂Cl₂. ^c Weak absorptions may be due to isomer b.Table III. ¹H and ¹³C NMR Data for New Compounds

	¹ H δ ^a	¹³ C				
		M(CO) ₅		Os(CO) _{5-x} (CNBu ^t) _x		
		δ(ax CO)	δ(eq CO) ^b	δ(CO) ^b		
Os(CO) ₄ (L)	1.53			187.4		
Os(CO) ₃ (L) ₂	1.48			193.4		
(OC) ₄ (L)OsCr(CO) ₅ (1-Cr)	1.55 ^c	229.6	222.7	187.1	180.0	165.4
(OC) ₄ (L)OsMo(CO) ₅ (1-Mo)	1.55 ^c	216.2	210.3	187.0	179.7	166.8
(OC) ₄ (L)OsW(CO) ₅ (1-W)	1.55 ^c	203.9 (176.1) ^d	202.3 (125.3) ^d	184.0	177.8	165.7
(OC) ₃ (L) ₂ OsCr(CO) ₅ (2a-Cr) ^e	1.47	231.7	225.5	194.1	168.0	
(OC) ₃ (L) ₂ OsCr(CO) ₅ (2b-Cr)	1.54	231.9	226.1	188.0	167.2	
(OC) ₃ (L) ₂ OsMo(CO) ₅ (2a-Mo) ^e	1.47	217.4	212.0	193.9	169.3	
(OC) ₃ (L) ₂ OsMo(CO) ₅ (2b-Mo) ^f	1.53	217.7	212.8	188.0	168.4	
(OC) ₃ (L) ₂ OsW(CO) ₅ (2a-W) ^e	1.47	205.9 (179.3) ^d	204.1 (125.7) ^d	190.5	168.3	
(OC) ₃ (L) ₂ OsW(CO) ₅ (2b-W)	1.53	206.2 (177.8) ^d	204.6 (125.5) ^d	185.3	167.3	

^a In CDCl₃ solution (room temperature). ^b ¹³CO-Enriched samples in CH₂Cl₂/CD₂Cl₂ at -30 or -40 °C. ^c Spectrum at -40 °C. ^d J_{W-C}. ^e Spectrum contained signals assigned to isomer b. ^f Spectrum contained a weak signal assigned to isomer a.

Herein, we report the syntheses of Os(CO)_{5-x}(Bu^tNC)_x (x = 1, 2) and their use in the preparation of (OC)_{5-x}(Bu^tNC)_xOsM(CO)₅ (M = Cr, Mo, W). Crystallographic and spectroscopic studies of these isocyanide derivatives reveal interesting differences to the phosphine analogues in that there is no evidence for the isomers with the isocyanide ligand trans to the metal-metal bond.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and dichloromethane were distilled under nitrogen from

potassium, potassium benzophenone ketyl, and P₂O₅, respectively. The carbonyls M(CO)₆ (M = Cr, Mo, W), Os₃(CO)₁₂, cyclooctene, and *tert*-butyl isocyanide were obtained commercially. Literature methods were used to prepare Os(CO)₅⁵ and M(CO)₅(THF).⁴ An external medium-pressure mercury discharge lamp (200 W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the irradiations. There was ~5 cm between the source and the edge of the reaction vessel.

Infrared spectra (Table II) were recorded on a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was periodically checked against the known absorption frequencies

of gaseous CO. Electron-impact (70-eV) mass spectra (Table I) were obtained with a Hewlett-Packard 5985 GC-MS instrument; the most intense peak of the ions of highest mass in each spectrum matched that calculated for the parent ion of the compound in question. NMR spectra (Table III) were recorded on either a Bruker WM400 spectrometer (operating frequencies: 400 MHz for ^1H and 100.6 MHz for ^{13}C) or a Bruker SY-100 spectrometer. The ^{13}C NMR spectra were obtained on samples enriched with ^{13}CO (~30%), which, in turn, were prepared from ^{13}CO -enriched $\text{M}(\text{CO})_5(\text{THF})$.⁴ The microanalyses (Table I) were obtained by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$. Method 1. The cyclooctene derivative $\text{Os}(\text{CO})_4(\eta^2\text{-cyclooctene})$ was prepared from $\text{Os}_3(\text{CO})_{12}$ by a procedure that is a modification of that of Burke:⁶ A quartz Carius tube fitted with a Teflon valve was charged with $\text{Os}_3(\text{CO})_{12}$ (138 mg, 0.152 mmol), cyclooctene (1.92 mL, 14.7 mmol), and benzene (60 mL). The vessel was cooled to -196°C and evacuated; the solution was degassed with one freeze-pump-thaw cycle. The vessel was pressurized with CO (1 atm) and the solution irradiated through a GWV filter ($\lambda \geq 370\text{ nm}$) for 23 h. The solvent and excess cyclooctene were removed on the vacuum line; the remaining solid was extracted with hexane ($2 \times 20\text{ mL}$). The extracts were combined and placed along with further hexane (35 mL) and Bu^tNC (64 μL , 0.57 mmol) in a round-bottom flask (~80-mL capacity) fitted with a Teflon valve. The flask was heated in the dark at $55\text{--}65^\circ\text{C}$ for 24 h. The solvent and excess Bu^tNC were removed on the vacuum line, and the remaining solid was subjected to sublimation at 25°C (0.1 mm) to a water-cooled probe whereupon $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ was obtained as a white solid. The yield of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ was 50 mg (28%).

Method 2. To a 100-mL three-necked flask were added $\text{Os}(\text{CO})_5$ (~155 mg, 0.47 mmol) in hexane/benzene (1/1, v/v, 50 mL), Bu^tNC (50 μL , 0.48 mmol), and the catalyst $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (~5 mg). The solution was refluxed for 20 min during which time the color of the solution changed from green to yellow. An infrared spectrum of the solution at this stage indicated the presence of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ and $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$, but not of $\text{Os}(\text{CO})_5$. The solvent and any remaining Bu^tNC were removed on the vacuum line, and the desired product was isolated as in method 1. The yield of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ was 52 mg (28%), that is, essentially the same as by method 1.

Preparation of $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$. To a 200-mL, three-necked flask were added $\text{Os}(\text{CO})_5$ (263 mg, 0.80 mmol) in hexane/benzene (1/1, v/v, 100 mL), Bu^tNC (70 μL , 0.67 mmol), and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (~5 mg). The solution was refluxed for 20 min at which time the flask and contents was cooled and more Bu^tNC (70 μL , 0.67 mmol) added; the solution was refluxed for a further 20 min. An infrared spectrum of the solution at this stage indicated the reaction was complete (the solution had turned from pale green to yellow). The solvent and any unreacted Bu^tNC were removed on the vacuum line. The remaining solid was extracted with hexane ($4 \times 20\text{ mL}$). The hexane extracts were combined and evaporated to dryness to yield crude $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ (80 mg, 23%). The analytical sample was obtained, as bright yellow, air-stable crystals, by sublimation (with some decomposition) of the crude product at $80\text{--}90^\circ\text{C}$ (0.1 mm) followed by recrystallization of the sublimed product from hexane.

Preparation of $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W). A solution of $\text{M}(\text{CO})_5(\text{THF})$ was prepared from $\text{M}(\text{CO})_6$ (M = Cr, 0.20 mmol; M = Mo, 0.60 mmol; M = W, 0.40 mmol) and THF (30 mL). The solution was reduced in volume to 1–2 mL and immediately cooled to -196°C . A solution of $\text{Os}(\text{CO})_2(\text{CNBu}^t)$ (40 mg, 0.10 mmol) in hexane (10 mL) was added to the frozen $\text{M}(\text{CO})_5(\text{THF})/\text{THF}$ and the resulting mixture allowed to warm with stirring. The treatment varied somewhat depending on the group 6 metal: For the chromium case the mixture was allowed to warm to room temperature, for molybdenum to 0°C , and for tungsten to room temperature followed by a further 20-min stirring. After this treatment, the isolation of the product was identical for each compound. The solvent was removed on the vacuum line and the residue extracted with hexane ($4 \times 10\text{ mL}$). The extracts were combined and evaporated to dryness. The

residue was subjected to sublimation under vacuum ($<0.02\text{ mm}$) at room temperature (M = Cr) or $\sim 40^\circ\text{C}$ (M = Mo, W) to a water-cooled probe that removed $\text{M}(\text{CO})_6$. The residue remaining after the sublimation was recrystallized from hexane/ CH_2Cl_2 (7/1) to give analytically pure $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$. The yields were 65–80% for M = Cr, 55–60% for M = Mo, and 30–40% for M = W. The chromium compound was bright yellow, the molybdenum compound colorless or pale yellow, and the tungsten compound pale yellow. All compounds could be handled in air for short periods without apparent decomposition; prolonged exposure did, however, result in decomposition.

Preparation of Isomer a of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W). A solution of $\text{M}(\text{CO})_5(\text{THF})$ in THF (30 mL) was prepared from $\text{M}(\text{CO})_6$ (M = Cr, 0.20 mmol; M = Mo, 0.55 mmol; M = W, 0.30 mmol). The solution was reduced in volume to 1–2 mL and cooled to -196°C . A solution of $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ (40 mg, 0.091 mmol) in hexane (10 mL) was added to the frozen $\text{M}(\text{CO})_5(\text{THF})/\text{THF}$. The solution was allowed to warm, with stirring, to room temperature (M = Cr), to 0°C (M = Mo), or to room temperature with further stirring at room temperature for 10 min (M = W). The solvent was then removed on the vacuum line. The residue was extracted repeatedly with hexane. The hexane extracts were combined and evaporated to dryness. The remaining solid (i.e., that had originally dissolved in hexane) was chromatographed on Florisil ($14 \times 1\text{ cm}$). Elution with hexane removed $\text{M}(\text{CO})_6$. The desired product, $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (mainly isomer a but with some of isomer b), was obtained by elution with hexane/ CH_2Cl_2 (4/1). The analytical samples were obtained by recrystallization from hexane/ CH_2Cl_2 (7/1). As such, the samples consisted mainly of isomer a but had some isomer b (~7%, M = Cr, W; ~20%, M = Mo).

The solid that remained after the hexane extraction described above was chromatographed on silica gel ($15 \times 1\text{ cm}$) with hexane/ CH_2Cl_2 (3/1) as the solvent to yield small amounts isomer b of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (see below).

In the tungsten case elution with hexane/ CH_2Cl_2 (1/1) gave a yellow band from which a yellow solid was isolated. The compound has not yet been completely characterized, but its properties suggest it has two unbridged dative metal-metal bonds analogous to the compound $(\text{OC})_3[\text{MeC}(\text{CH}_2\text{O})_3\text{P}]_2\text{OsOs}(\text{CO})_4\text{W}(\text{CO})_5$ recently reported from this laboratory.⁷

The (combined isomer a and b) yields and colors of the $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ complexes were similar to those for the analogous $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ derivatives given above.

Preparation of Isomer b of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W). A saturated solution of isomer a of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ in hexane was prepared in an 80-mL round-bottom flask fitted with a Teflon valve. The solution was degassed by three freeze-pump-thaw cycles. The solution was then stirred in the dark at room temperature for 7–10 days. During this time the less soluble isomer b precipitated from solution. The supernatant solution was removed, and the precipitate was washed several times with hexane to remove traces of isomer a and dried on the vacuum line. In the case of the molybdenum complex partial decomposition to a black material accompanied the isomerization. The desired product was separated from the decomposition product by dissolving it in hexane/ CH_2Cl_2 (3/1) and passing the solution through a short column ($1 \times 1\text{ cm}$) of silica gel. Removal of the solvent on the vacuum line gave the crude product. The analytical samples of the $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W) complexes were obtained by recrystallization from hexane/ CH_2Cl_2 . As such they were pure isomer b as indicated by ^{13}C NMR spectroscopy.

Determination of the Isomer Ratio at Equilibrium for the $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ (M = Cr, Mo, W) Complexes. Recrystallized isomer b of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ was dissolved in CH_2Cl_2 contained in a round-bottom flask fitted with a Teflon valve. The solution was degassed with a freeze-pump-thaw cycle. The solution was stirred under vacuum in the dark at room temperature. The isomerization was monitored by ^1H NMR spectroscopy and infrared spectroscopy until it had been judged that the equilibrium had been attained. This took approximately 2 days for the molybdenum derivative and 5–10 days for the

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chromium and tungsten analogues. After this period the solvent was removed under reduced pressure. The remaining solid was dissolved in CDCl_3 , and a ^1H NMR spectrum of the solution was recorded at room temperature. The a/b ratio was obtained from the areas of the ^1H NMR signal of each isomer. The approximate a/b isomer ratios were 1/2.6, 1/1.8, and 1/2.3 for the chromium, molybdenum, and tungsten derivatives, respectively. It was verified for the chromium and molybdenum compounds that the equilibrium ratio could be obtained under the same conditions starting from predominantly the a isomer.

Reaction of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ with $\text{Cr}(\text{CO})_5(\text{CNBu}^t)(\text{THF})$. A hexane solution of Bu^tNC was added to an approximately equimolar quantity of $\text{Cr}(\text{CO})_5(\text{THF})$ maintained at -196°C . The frozen mixture was warmed to room temperature and the solvent removed on the vacuum line. The residue was sublimed at room temperature (<0.02 mm) to a probe at -78°C to give a pale yellow solid identified by infrared spectroscopy as $\text{Cr}(\text{CO})_5(\text{CNBu}^t)$.⁸ A solution of $\text{Cr}(\text{CO})_5(\text{CNBu}^t)$ in THF was placed in a Pyrex Carius tube fitted with a Teflon valve; the solution was degassed with two freeze-pump-thaw cycles. The stirred solution was then subjected to UV irradiation at room temperature. The conversion of $\text{Cr}(\text{CO})_5(\text{CNBu}^t)$ to $\text{Cr}(\text{CO})_4(\text{CNBu}^t)(\text{THF})$ was monitored by IR spectroscopy. A small amount of $\text{Cr}(\text{CO})_5(\text{THF})$ was also produced. When the conversion was judged complete, the solution was reduced in volume and cooled to -196°C . A hexane solution of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ was added to the frozen solution of $\text{Cr}(\text{CO})_4(\text{CNBu}^t)(\text{THF})$. An approximate molar ratio for $\text{Os}(\text{CO})_4(\text{CNBu}^t)/\text{Cr}(\text{CO})_4(\text{CNBu}^t)(\text{THF})$ of 1/2 was employed. The frozen mixture was warmed to room temperature with stirring at which point the solvent was removed under vacuum. The remaining solid was chromatographed on a silica gel column. Elution with hexane removed unreacted $\text{Cr}(\text{CO})_5(\text{CNBu}^t)$. Elution with hexane/ CH_2Cl_2 (5/1, v/v) separated a yellow band that was collected in three fractions. The first fraction contained mostly $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsCr}(\text{CO})_5$ (1-Cr). The remaining two fractions also contained small amounts of 1-Cr besides the desired product. The impurity of 1-Cr was removed by washing the solid several times with hexane. The bright yellow residue was identified as $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsCr}(\text{CO})_5$, 2b-Cr (i.e., the thermodynamically preferred isomer). The yield was estimated to be $\sim 60\%$.

X-ray Analysis of $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsCr}(\text{CO})_5$ (1-Cr) and $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsCr}(\text{CO})_5$ (2b-Cr). Crystals of 1-Cr and 2b-Cr were mounted on an Enraf Nonius CAD-4F diffractometer equipped with a commercial low-temperature attachment that had been extensively modified in house. Intensity data (Mo $K\alpha$ /graphite monochromator) were measured at -73°C (1-Cr) and 22°C (2b-Cr). The unit cells were determined from 25 well-centered reflections (1-Cr, $19^\circ \leq \theta \leq 22^\circ$; 2b-Cr, $14^\circ \leq \theta \leq 17^\circ$). Two intensity standards were measured every 1 h (1-Cr) or 1.5 h (2b-Cr) of acquisition time. The intensity data of 1-Cr showed no significant variation, whereas those of 2b-Cr decayed systematically by 2% during the course of data acquisition. The data were corrected analytically for absorption.⁹ Data reductions were performed, which included intensity scaling and Lorentz and polarization corrections.

The structure of 1-Cr was solved from the Patterson map and subsequent Fourier syntheses. The methyl carbon atoms of the *tert*-butyl group were found to occur in general positions resulting in two 50% occupied orientations of this group related to one another by a crystallographic mirror plane bisecting the molecule. (This disorder could not be eliminated by refinement in the space group $Pna2_1$.) The refined anisotropic atomic thermal parameters suggest that the disorder may involve more than just the rotational conformation of the *tert*-butyl group; however, the overall good agreement indicates that refinement of a more complex model was not justified for our purposes. The 50% occupancy hydrogen atoms were initially placed in calculated positions of 0.95 Å from their respective carbon atoms. Final full-matrix, least-squares refinement included allowed coordinates for all atoms (subject to distance and angle restraints that imposed approximate tetrahedral geometry about the carbon atoms of the *tert*-butyl group), anisotropic thermal parameters for Os, Cr, O, and the methyl

Table IV. Crystallographic Data for the Structure Determinations for 1-Cr and 2b-Cr

	1-Cr	2b-Cr
formula	$\text{C}_{14}\text{H}_9\text{CrNO}_5\text{Os}$	$\text{C}_{18}\text{H}_{18}\text{CrN}_2\text{O}_8\text{Os}$
fw	577.44	632.56
space group	$Pnam$	$P2_1/n$
cryst syst	orthorhombic	monoclinic
a, Å	20.272 (4)	9.129 (1)
b, Å	9.648 (1)	12.258 (1)
c, Å	9.843 (2)	20.863 (3)
β , deg		90.32 (1)
V, Å ³	1925.0	2334.6
Z	4	4
d_{calc} , g cm ⁻³	1.992	1.800
temp, °C	-73	22
cryst size, mm	0.20 × 0.22 × 0.40	0.08 × 0.14 × 0.26
transmission coeff	0.25–0.30	0.40–0.62
$\mu(\text{Mo } K\alpha)$, cm ⁻¹	71.94	59.4
$\lambda(\text{Mo } K\alpha)$, Å	0.71069	0.71069
min-max 2θ , deg	5–50	4–49
R_f^a	0.027 ^b	0.026 ^c
R_{wt}^d	0.027 ^e	0.022 ^f

^a $R_f = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b 1306 observed data, $I \geq 2.5\sigma(I)$. ^c 2505 observed data, $I \geq 2.5\sigma(I)$. ^d $R_{\text{wt}} = [\sum(w(|F_o| - |F_c|)^2) / \sum(wF_o^2)]^{1/2}$. ^e $w = [12.7869t_0(x) + 17.1586t_1(x) + 8.08044t_2(x)]^{-1}$, where $x = |F_o|/F_{\text{max}}$ and t_n are the polynomial functions of the Chebyshev series.³⁶ ^f $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$.

carbon atoms, isotropic temperature factors for the remaining non-hydrogen atoms, and a single isotropic temperature factor for the H atoms. The maximum |shift/esd| was 0.01 for the final cycle of refinement of 135 parameters for 1306 observations ($I_o \geq 2.5\sigma(I_o)$) and 42 restraints. The largest peak in the final difference map was 0.9 (3) Å⁻³. An empirical weighting scheme was applied such that $(w(|F_o| - |F_c|)^2)$ was near constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$.

The structure of 2b-Cr was also solved from its Patterson map and subsequent Fourier syntheses. The hydrogen atoms were included in calculated positions with assigned isotropic temperature factors and were repositioned after further structure refinement. Final full-matrix, least-squares refinement included coordinates for all non-hydrogen atoms and an extinction coefficient.¹⁰ The maximum |shift/esd| was 0.05 for the final cycle of refinement of 202 parameters for 2505 observations ($I_o \geq 2.5\sigma(I_o)$). The largest peak in the final difference map was 1.0 (1) e Å⁻³. A weighting scheme, based on counting statistics, was applied such that $(w(|F_o| - |F_c|)^2)$ was near constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$.

Complex scattering factors for neutral atoms were used in the calculation of structure factors.¹¹ The computer programs used for data reduction, structure solution, and initial refinement were from the NRCVAX Crystal Structure System.¹² The program suite CRYSTALS¹³ was employed in the final stages of the refinement of the structure of 1-Cr that involved the use of restraints. All computations were carried out on a MicroVAX-II computer. Crystallographic data are summarized in Table IV. Fractional coordinates and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms of 1-Cr and 2b-Cr are listed in Tables V and VI, respectively. Bond lengths and selected angles for 1-Cr and 2b-Cr are given in Table VII and VIII, respectively. Other crystallographic data are deposited as supplementary material.

Results and Discussion

$\text{Os}(\text{CO})_{5-x}(\text{CNBu}^t)_x$ ($x = 1, 2$) Compounds. The iso-

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Table V. Fractional Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^4$) for the Non-Hydrogen Atoms of 1-Cr at -73°C

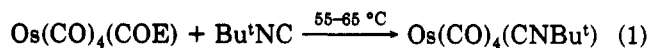
atom	x/a	y/b	z/c	$U(\text{iso})$
Os	8456.0 (2)	9156.9 (4)	7500	364
Cr	8843.5 (6)	12122 (2)	7500	355
O(1)	9954 (3)	8595 (10)	7500	574
O(2)	7915 (4)	6160 (8)	7500	771
O(3)	8505 (3)	9705 (6)	4412 (5)	649
O(4)	9286 (4)	15074 (8)	7500	678
O(5)	7806 (2)	12754 (7)	5355 (6)	665
O(6)	9907 (2)	11607 (6)	5393 (6)	664
N	6949 (4)	10064 (7)	7500	432 (19)
C(1)	9401 (5)	8811 (10)	7500	462 (24)
C(2)	8142 (5)	7264 (13)	7500	578 (27)
C(3)	8493 (3)	9502 (6)	5527 (7)	451 (15)
C(4)	9096 (5)	13927 (10)	7500	470 (23)
C(5)	8195 (3)	12478 (8)	6156 (7)	497 (16)
C(6)	9488 (3)	11765 (7)	6148 (7)	443 (16)
C(7)	7511 (4)	9788 (10)	7500	390 (21)
C(8)	6235 (3)	10301 (8)	7500	535 (25)
C(9)	5932 (5)	9121 (12)	6802 (7)	798
C(10)	6024 (4)	10386 (11)	8950 (8)	822
C(11)	6119 (5)	11605 (11)	6776 (7)	798

^aGeneral equivalent positions: (x, y, z) , $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, $(-x, -y, \frac{1}{2} + z)$, $(-x, -y, -z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$, $(x, y, \frac{1}{2} - z)$.

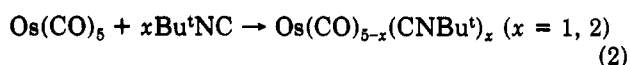
Table VI. Fractional Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Thermal Parameters (\AA^2) for the Non-Hydrogen Atoms of 2b-Cr

atom	x/a	y/b	z/c	B_{iso}
Os	0.09352 (3)	0.08713 (3)	0.11570 (2)	3.218
Cr	0.28757 (12)	0.27805 (10)	0.13772 (6)	3.82
O(3)	-0.0807 (6)	-0.1215 (4)	0.0932 (3)	6.5
O(4)	0.3135 (6)	0.0515 (5)	0.0074 (3)	6.5
O(5)	0.3101 (6)	-0.0094 (5)	0.2124 (3)	6.4
O(6)	0.0126 (5)	0.4119 (5)	0.1542 (3)	5.5
O(7)	0.2978 (7)	0.2370 (5)	0.2811 (3)	7.3
O(8)	0.5594 (6)	0.1388 (5)	0.1228 (3)	7.0
O(9)	0.4615 (7)	0.4803 (5)	0.1596 (3)	8.5
O(10)	0.2825 (7)	0.3268 (5)	-0.0042 (3)	7.0
N(1)	-0.1066 (6)	0.2394 (5)	0.0292 (3)	3.84 (12)
N(2)	-0.1037 (6)	0.1768 (5)	0.2289 (3)	3.87 (12)
C(1)	-0.0305 (7)	0.1826 (6)	0.0588 (3)	3.37 (14)
C(2)	-0.0308 (7)	0.1425 (6)	0.1885 (3)	3.41 (14)
C(3)	-0.0218 (9)	-0.0391 (7)	0.1018 (4)	4.7 (2)
C(4)	0.2312 (8)	0.0667 (6)	0.0473 (4)	4.7 (2)
C(5)	0.2255 (8)	0.0301 (6)	0.1758 (4)	4.5 (2)
C(6)	0.1137 (8)	0.3594 (6)	0.1489 (4)	4.3 (2)
C(7)	0.2909 (8)	0.2502 (7)	0.2271 (4)	4.7 (2)
C(8)	0.4547 (8)	0.1897 (6)	0.1273 (4)	4.4 (2)
C(9)	0.3969 (9)	0.4008 (7)	0.1510 (4)	5.1 (2)
C(10)	0.2840 (8)	0.3069 (6)	0.0500 (4)	4.6 (2)
C(11)	-0.2049 (8)	0.3105 (6)	-0.0073 (4)	4.3 (2)
C(12)	-0.1944 (8)	0.2252 (6)	0.2791 (3)	4.0 (2)
C(13)	-0.2785 (9)	0.3866 (7)	0.0404 (4)	6.4
C(14)	-0.3165 (10)	0.2393 (8)	-0.0403 (4)	7.4
C(15)	-0.1162 (11)	0.3729 (8)	-0.0549 (4)	7.7
C(16)	-0.2787 (10)	0.3168 (7)	0.2495 (4)	6.5
C(17)	-0.0930 (9)	0.2623 (9)	0.3310 (4)	7.7
C(18)	-0.2935 (10)	0.1375 (8)	0.3039 (5)	7.4

cyanide derivatives $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ and $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ were prepared by methods summarized in eqs 1 and 2.



COE = cyclooctene



The reactions indicated eq 2 were carried out in hexane/benzene at reflux temperature with a catalyst of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. This method has been previously used in the preparation of the iron analogues.¹⁴ The pattern of the

Table VII. Bond Lengths (\AA) and Selected Angles (deg) for 1-Cr

Bond Lengths			
Os-Cr	2.966 (2)	Os-C(1)	1.945 (10)
Os-C(2)	1.934 (12)	Os-C(3)	1.972 (7)
Os-C(7)	2.011 (9)	Cr-C(4)	1.815 (10)
Cr-C(5)	1.896 (7)	Cr-C(6)	1.896 (7)
C(1)-O(1)	1.139 (11)	C(2)-O(2)	1.160 (13)
C(3)-O(3)	1.115 (8)	C(4)-O(4)	1.172 (12)
C(5)-O(5)	1.146 (8)	C(6)-O(6)	1.139 (7)
N-C(7)	1.169 (11)	N-C(8)	1.466 (10)
C(8)-C(9)	1.464 ^a	C(8)-C(10)	1.492 ^a
C(8)-C(11)	1.465 ^a		
Angles			
C(1)-Os-Cr	84.5 (3)	C(2)-Os-Cr	176.2 (3)
C(2)-Os-C(1)	99.3 (4)	C(3)-Os-Cr	80.0 (2)
C(3)-Os-C(1)	89.5 (3)	C(3)-Os-C(2)	99.9 (2)
C(7)-Os-Cr	87.7 (3)	C(7)-Os-C(1)	172.2 (4)
C(7)-Os-C(2)	88.4 (4)	C(3)-Os-C(3') ^b	160.0 (3)
C(7)-Os-C(3)	89.2 (4)	C(4)-Cr-Os	179.0 (3)
C(5)-Cr-Os	89.5 (2)	C(5)-Cr-C(4)	91.2 (3)
C(5)-Cr-C(5') ^b	88.5 (4)	C(6)-Cr-Os	90.4 (2)
C(6)-Cr-C(4)	88.9 (3)	C(6)-Cr-C(5)	91.2 (3)
C(6)-Cr-C(5') ^b	179.6 (3)	C(6)-Cr-C(6') ^b	89.2 (4)
C(8)-N-C(7)	175.8 (7)	O(1)-Cr(1)-Os	179.3 (10)
O(2)-C(2)-Os	175.8 (9)	O(3)-C(3)-Os	179.0 (7)
O(4)-C(4)-Cr	177.2 (9)	O(5)-C(5)-Cr	177.0 (7)
O(6)-C(6)-Cr	174.8 (6)	N-C(7)-Os	175.5 (8)
C(9)-C(8)-N	170.0 ^a	C(10)-C(8)-N	106.9 ^a
C(10)-C(8)-C(9)	111.8 ^a	C(11)-C(8)-N	107.0 ^a
C(11)-C(8)-C(9)	111.9 ^a	C(11)-C(8)-C(10)	111.9 ^a

^aParameters subjected to restraints during refinement. ^bPrime ([']) = $(x, y, 1.5 - z)$.

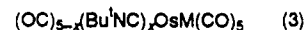
CO stretches in the infrared spectrum of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ in hexane (Table II) is typical for an $\text{M}(\text{CO})_4(\text{L})$ compound that has trigonal-bipyramidal coordination about M with L in an axial position.¹⁴⁻¹⁸ Similarly, the single infrared-active carbonyl stretch exhibited by $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ in hexane is consistent with trigonal-bipyramidal coordination about the osmium atom with the isocyanide ligands in the axial sites.^{14-16,19}

$(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ ($\text{M} = \text{Cr}, 1\text{-Cr}; \text{M} = \text{Mo}, 1\text{-Mo}; \text{M} = \text{W}, 1\text{-W}$) Complexes. These complexes were prepared by the method indicated in eq 3 ($x = 1$). The complexes are moderately stable in air and are bright yellow ($\text{M} = \text{Cr}$), pale yellow ($\text{M} = \text{Mo}$), and white ($\text{M} = \text{W}$).



$x = 1: \text{M} = \text{Cr}, \text{Mo}, \text{W}$

$x = 2$



1-Cr, 1-Mo, 1-W

2-Cr, 2-Mo, 2-W

The structure of 1-Cr was determined by X-ray crystallography. A view of the molecule is shown in Figure 1; bond length and angle data are given in Table VII. As can be seen from the figure, the 18-electron compound $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ acts as a 2-electron donor ligand toward the

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Table VIII. Bond Lengths (Å) and Selected Angles (deg) for 2b-Cr

Bond Lengths			
Os-Cr	2.9693 (12)	Os-C(3)	1.894 (9)
Os-C(1)	2.011 (7)	Os-C(4)	1.923 (8)
Os-C(2)	2.018 (7)	Os-C(5)	1.869 (8)
Cr-C(6)	1.890 (8)	Cr-C(9)	1.825 (9)
Cr-C(7)	1.897 (8)	Cr-C(10)	1.864 (8)
Cr-C(8)	1.884 (8)	C(7)-O(7)	1.138 (10)
C(3)-O(3)	1.158 (10)	C(8)-O(8)	1.146 (10)
C(4)-O(4)	1.140 (10)	C(9)-O(9)	1.153 (10)
C(5)-O(5)	1.187 (9)	C(10)-O(10)	1.156 (10)
C(6)-O(6)	1.130 (9)	C(2)-N(2)	1.156 (9)
C(1)-N(1)	1.160 (9)	N(2)-C(12)	1.466 (9)
N(1)-C(11)	1.462 (9)	C(12)-C(16)	1.493 (11)
C(11)-C(13)	1.522 (12)	C(12)-C(17)	1.491 (11)
C(11)-C(14)	1.505 (11)	C(12)-C(18)	1.499 (12)
C(11)-C(15)	1.496 (12)		
Angles			
Cr-Os-C(1)	88.05 (19)	C(1)-Os-C(5)	166.4 (3)
Cr-Os-C(2)	87.46 (19)	C(2)-Os-C(3)	94.3 (3)
Cr-Os-C(3)	177.14 (24)	C(2)-Os-C(4)	167.0 (3)
Cr-Os-C(4)	79.96 (23)	C(2)-Os-C(5)	89.1 (3)
Cr-Os-C(5)	78.99 (24)	C(3)-Os-C(4)	98.4 (3)
C(1)-Os-C(2)	86.1 (3)	C(3)-Os-C(5)	98.8 (3)
C(1)-Os-C(3)	94.3 (3)	C(4)-Os-C(5)	91.6 (3)
C(1)-Os-C(4)	90.3 (3)	C(6)-Cr-C(9)	90.3 (3)
Os-Cr-C(6)	86.22 (23)	C(6)-Cr-C(10)	90.6 (3)
Os-Cr-C(7)	90.94 (25)	C(7)-Cr-C(8)	90.1 (3)
Os-Cr-C(8)	90.69 (23)	C(7)-Cr-C(9)	89.7 (3)
Os-Cr-C(9)	176.5 (3)	C(7)-Cr-C(10)	179.4 (3)
Os-Cr-C(10)	89.45 (24)	C(8)-Cr-C(9)	92.8 (3)
C(6)-Cr-C(7)	89.0 (3)	C(8)-Cr-C(10)	90.3 (3)
C(6)-Cr-C(8)	176.8 (3)	C(9)-Cr-C(10)	89.9 (3)
C(1)-N(1)-C(11)	178.9 (7)	C(2)-N(2)-C(12)	177.4 (7)
Os-C(1)-N(1)	176.0 (6)	Os-C(2)-N(2)	177.8 (6)
Os-C(3)-O(3)	173.9 (7)	Os-C(5)-O(5)	177.5 (7)
Os-C(4)-O(4)	177.9 (7)	Cr-C(8)-O(8)	177.1 (7)
Cr-C(6)-O(6)	176.9 (7)	Cr-C(9)-O(9)	177.6 (7)
Cr-C(7)-O(7)	176.8 (7)	Cr-C(10)-O(10)	178.7 (7)
N(1)-C(11)-C(13)	107.3 (6)	N(2)-C(12)-C(16)	107.5 (6)
N(1)-C(11)-C(14)	107.8 (6)	N(2)-C(12)-C(17)	107.0 (6)
N(1)-C(11)-C(15)	108.5 (6)	N(2)-C(12)-C(18)	107.5 (6)
C(13)-C(11)-C(14)	110.7 (7)	C(16)-C(12)-C(17)	112.8 (7)
C(13)-C(11)-C(15)	113.7 (7)	C(16)-C(12)-C(18)	111.8 (7)
C(14)-C(11)-C(15)	111.7 (7)	C(17)-C(12)-C(18)	110.0 (7)

chromium atom in the $\text{Cr}(\text{CO})_5$ fragment via an unbridged, dative metal-metal bond. The isocyanide ligand is *cis* to the metal-metal bond, which is in contrast to $(\text{Me}_3\text{P})(\text{OC})_4\text{OsCr}(\text{CO})_5$ (**3**) where the phosphine ligand is *trans* to the osmium-chromium bond.⁴ The Os-Cr bond length in **1-Cr** is 2.966 (2) Å whereas in **3** it is 2.979 (2) Å. Although the difference is small, it does suggest that $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ is a better donor ligand to $\text{Cr}(\text{CO})_5$ than is $\text{Os}(\text{CO})_4(\text{PMe}_3)$. This is contrary to expectation, given that PMe_3 is a better donor ligand than Bu^tNC . (The CO stretching frequencies of 2061, 1980, and 1939 cm^{-1} of $\text{Os}(\text{CO})_4(\text{PMe}_3)$ ¹⁸ may be compared to the corresponding values given in Table II for $\text{Os}(\text{CO})_4(\text{CNBu}^t)$.) A similar situation was observed for the dative Os-Os bond lengths in $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsOs}_3(\text{CO})_{11}$ and $(\text{Me}_3\text{P})(\text{OC})_4\text{OsOs}_3(\text{CO})_{11}$.²⁰ At that time, it was rationalized that with the better π -acceptor ligand CO *trans* to the dative metal-metal bond the repulsive interactions between the filled metal d orbitals across the bond was lessened. Furthermore, with the non-carbonyl ligand and the 16-electron unit in a *cis* configuration, the system avoids as far as possible the better π -acceptor carbonyl ligands competing for the same π -electron density on the osmium atom. The same arguments can, of course, be applied to **1-Cr** and **3**.

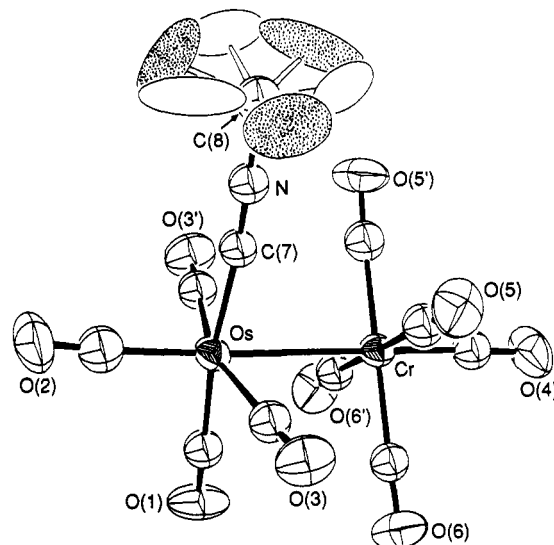


Figure 1. Molecular structure of $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsCr}(\text{CO})_5$ (**1-Cr**). The disorder in the Bu^t group is shown.

As observed in other molecules with unbridged dative metal-metal bonds,^{3,4} there is an inward leaning of the equatorial ligands on the donor half of the molecule (e.g., $\text{Cr-Os-C}(3) = 80.0 (2)^\circ$). This inward leaning is not present in the equatorial carbonyls of the acceptor half of the molecule (e.g., $\text{Os-Cr-C}(6) = 90.4 (2)^\circ$). The Cr-C distance (1.815 (10) Å) *trans* to the metal-metal bond is significantly shorter than the two other independent Cr-C distances (both 1.896 (7) Å). This has been observed in other complexes with dative metal-metal bonds⁴ and is taken to indicate that the 18-electron compound is a weak donor ligand. A repulsive π interaction between the d orbitals on the metal atoms would also be expected to increase the metal to carbonyl $d\pi$ to π^* bonding to the *trans* carbonyl and thus shorten the Cr-C bond to that carbonyl. A repulsive π interaction between the metal d orbitals would also be expected to shorten the Os-C bond *trans* to the dative Os-Cr bond, but this bond is not significantly shorter than the radial Os-C bonds. The dimensions of the $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ ligand are similar to those of the $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ ligand in $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsOs}_3(\text{CO})_{11}$.²⁰

The spectroscopic properties of the $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ complexes are consistent with these complexes having the same structure in solution as that found for **1-Cr** in the solid state. The two signals in an intensity ratio of 1/4 in the 230–200 ppm region of the ^{13}C NMR of the $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ complexes (Table III) are readily assigned to the axial and radial carbonyls, respectively, of the $\text{M}(\text{CO})_5$ moiety. There is the typical upfield shift on going to the derivative with the group 6 metal lower in the periodic table.²¹ The signals due to the carbonyls bound to tungsten show the expected coupling to ^{183}W .

In the 190–160 ppm region of the spectra there are three signals in an approximate 2/1/1 ratio as expected for an $\text{Os}(\text{CNBu}^t)(\text{CO})_4$ moiety with the isocyanide ligand in a *cis* position to the OsM bond (Table III). The signal to highest field is attributed to the carbonyl ligand *trans* to the dative metal-metal bond. In all complexes we have prepared that contain a carbonyl ligand *trans* to a dative metal-metal bond, the ^{13}C NMR resonance of this carbonyl carbon occurs at unusually high fields.^{1,4,20,22} In the spectra

(20) Einstein, F. W. B.; Johnston, V. J.; Ma, A. K.; Pomeroy, R. K. *Organometallics* 1990, 9, 52.

(21) (a) Bodner, G. M. *Inorg. Chem.* 1975, 14, 2694. (b) Mann, B. E.; Taylor, B. F. ^{13}C NMR Data for Organometallic Compounds; Academic: New York, 1981; p 14.

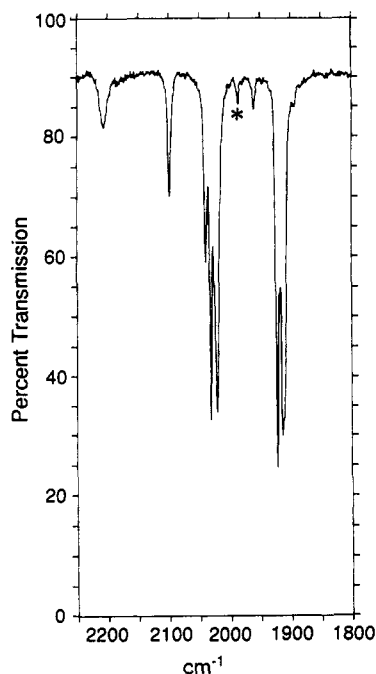


Figure 2. Infrared spectrum, in the 1800–2250-cm⁻¹ region, of 1-Cr in hexane. The peak marked with an asterisk is due to Cr(CO)₆.

of the (CO)₄(R₃P)OsM(CO)₅ derivatives (i.e., the minor isomer with the PR₃ ligand cis to the Os–M bond) the assignment of the signals due to the Os(PR₃)(CO)₄ fragment is unambiguous because of the small cis and large trans couplings to the phosphorus atom.⁴ The other signal of intensity 1 in the spectra of the (OC)₄(Bu^tNC)OsM(CO)₅ complexes is therefore assigned to the carbonyl trans to the Bu^tNC ligand and that of intensity 2 to the carbonyls cis to this ligand.

Unlike the (R₃P)(OC)₄OsM(CO)₅ complexes, the isocyanide analogues are slightly soluble in hexane such that infrared spectra with well-resolved CO stretching vibrations can be obtained. The infrared spectrum of 1-Cr in hexane is shown in Figure 2; the corresponding spectra of 1-Mo and 1-W are given in Figure 3. Comparison of these spectra with those of (η⁵-C₅Me₅)(OC)₂IrW(CO)₅² and (R₃P)(OC)₄OsM(CO)₅⁴ leads to the conclusion that the bands below 2000 cm⁻¹ can be associated with vibrations that mainly involve the carbonyls of the M(CO)₅ unit and the bands in the 2000–2125-cm⁻¹ region as mainly due to the carbonyls of the Os(CO)₄(L) (L = PR₃ or CNBu^t) or (η⁵-C₅Me₅)Ir(CO)₂ unit. This is consistent with the expected polarity of the donor–acceptor metal–metal bond of (δ⁺)Os → M(δ⁻). The carbonyl (and isocyanide) stretching frequencies shift to higher values on going from the free Os(CO)₄(CNBu^t) molecule to the coordinated state (Table II), consistent with less back-bonding to the CO (and CNBu^t) groups in the latter state.

The *cis*-Os(CO)₄(X)(Y) and M(CO)₅(L') fragments are expected to have four and three infrared-active CO stretches, respectively.²³ This is observed for 1-Cr (Figure 2) although the CO stretch at the lowest frequency does have a shoulder. The spectra of 1-Mo and 1-W (Figure 3), however, show more than the expected number of bands. For the M(CO)₅(L') unit the extra bands could be due to lowering of the C_{4v} symmetry of the unit due to the asymmetry of the L' ligand. This cannot be the case for

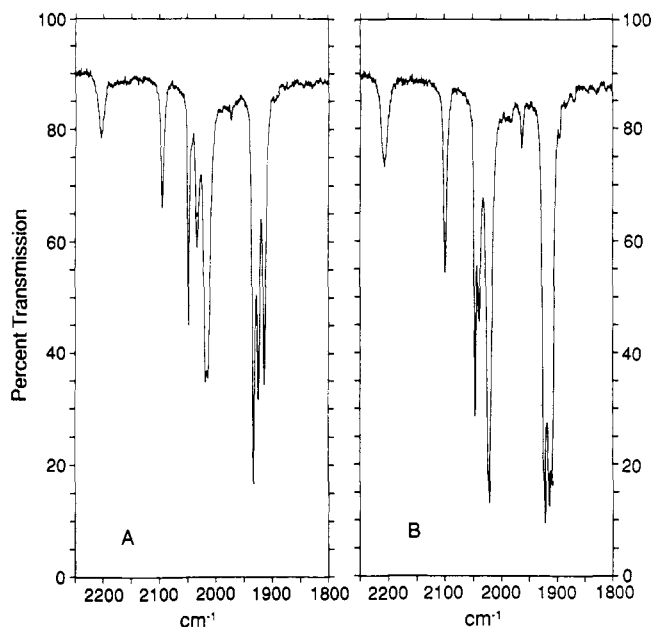


Figure 3. Infrared spectrum, in the 1800–2250-cm⁻¹ region, of 1-Mo (A) and 1-W (B) (both samples in hexane).

the Os(CO)₄(X)(Y) fragment since four carbonyl stretches are the maximum number allowed, no matter what the symmetry of X and Y. (The ¹³C NMR spectrum of 1-Mo clearly shows there is only one isomer present in solution.)

We believe the splitting of the lowest carbonyl stretching absorption of the Os(CO)₄ unit in 1-Mo can be attributed to the presence of different conformers of 1-Mo in solution. It is well-known that different conformers of a molecule can give rise to splitting of the carbonyl stretching absorptions in the infrared spectra of metal carbonyl compounds.²⁴ In one conformer of 1-Mo a methyl group could eclipse the axial CO bound to the osmium atom, whereas in the second conformer two of the methyl groups could be in staggered positions with respect to this carbonyl. This could give rise to the observed splitting of only one CO stretching band due to the Os(CO)₄ unit in the infrared spectrum. This is because only the vibration that involves mainly the axial carbonyl on osmium would be significantly affected; the other CO stretching vibrations of the two conformers might be expected to be degenerate. This effect should also be observable for the CO stretching vibrations of the M(CO)₅ portion of the molecules since the methyl groups have different orientations with respect to the equatorial carbonyls on M in each conformer. Consistent with this view, the molybdenum complex, which is the only derivative that shows five bands for the Os(CO)₄ portion of the molecule, also shows an extra absorption that is clearly resolved in the 1900–1950 cm⁻¹ region, the region associated with vibrations that involve mainly the carbonyls of the M(CO)₅ unit (Figure 3). Although there are two conformers present in the solid-state structure of 1-Cr (Figure 1), in the model used in the structure refinement the conformers are enantiomers and they would therefore give the same infrared spectrum if they were present in solution.

There is no evidence in the ¹³C NMR spectra of the (OC)₄(Bu^tNC)OsM(CO)₅ complexes for the isomer with the isocyanide ligand trans to the dative metal–metal bond. This is in contrast to the (R₃P)(OC)₄OsM(CO)₅ complexes where the isomer with the phosphine or phosphite ligand

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(23) See, for example, ref 16, pp 98–101.

(24) (a) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* 1967, 89, 2773. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1037.

trans to the metal-metal bond is the major, or only, isomer present in solution.⁴ The crystal structures of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) complexes show this isomer is also adopted in the solid state.⁴

This behavior parallels that for metal carbonyl compounds with nondative metal-metal bonds. For example, in compounds of the type $\text{M}'_2(\text{CO})_{10-x}(\text{L}')_x$ ($\text{M}' = \text{Mn}, \text{Re}$; $\text{L}' = \text{PR}_3$, $x = 1, 2$; $\text{L}' = \text{CNR}$, $x = 1-4$), when L' is a phosphorus donor ligand, these ligands are found in both equatorial and axial sites with large PR_3 ligands preferring the less hindered axial sites.²⁵ For the derivatives with $\text{L}' = \text{RNC}$, the isocyanide ligands are found exclusively in the equatorial positions.²⁶ Similarly, in cluster complexes of the type $\text{Os}_3(\text{CO})_{12-x}(\text{L}')_x$ ($x = 1-6$), phosphorus donor ligands are invariably found in equatorial sites²⁷ whereas isocyanide ligands usually adopt axial sites.²⁸ These results can be rationalized if the axial site is electronically preferred but the equatorial site is sterically favored.

In solution at room temperature the isomers of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ were shown to be in dynamic equilibrium by the spin saturation transfer technique. This and other observations for these complexes were consistent with the isomerization proceeding via an intermediate with bridging carbonyls, which also exchanges the carbonyls on osmium and tungsten.⁴ When the $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ complexes were prepared from ^{13}C -enriched $\text{M}(\text{CO})_5(\text{THF})$ and unenriched $\text{Os}(\text{CO})_4(\text{CNBu}^t)$, it was found that the $[^{13}\text{C}]$ carbonyls were scrambled over both the Os and M sites. This is also consistent with terminal-bridge carbonyl exchange, although as pointed out for $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsOs}_3(\text{CO})_{11}$ there must be a second process that exchanges the carbonyl trans to the Bu^tNC ligand with the other carbonyls.²⁰

The isocyanide ligand is also known to readily act as a bridging ligand,²⁹ but there was no evidence for isomers of $(\text{OC})_4(\text{Bu}^t\text{NC})\text{OsM}(\text{CO})_5$ with the Bu^tNC ligand bound to the group 6 metal atom. To ascertain if this was due to kinetic or thermodynamic reasons, the reaction of $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ with $\text{Cr}(\text{CO})_4(\text{CNBu}^t)(\text{THF})$ was carried out. The product was identified spectroscopically as $[\text{cis-dieq}-(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{Os}]\text{Cr}(\text{CO})_5$ (**2b-Cr**, see below). The cis, diequatorial rather than the trans, diequatorial isomer (**2a-Cr**, see below) is the expected product if the isocyanide migration occurs via an intermediate that has a carbonyl ligand (from the osmium moiety) and the isocyanide ligand bridging in a plane that is perpendicular to the $\text{Os}-\text{CNBu}^t$ bond.

It is concluded that the isomer with the isocyanide ligand located on the donor metal atom is thermodynamically

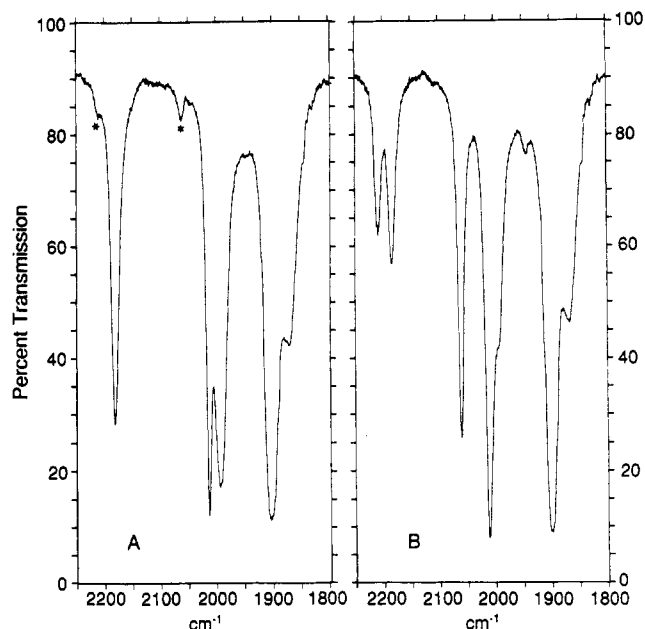
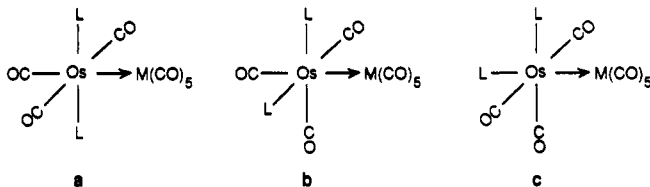


Figure 4. Infrared spectrum, in the $1800\text{--}2250\text{-cm}^{-1}$ region, of **2a-Cr** (A) and **2b-Cr** (B) (both samples in CH_2Cl_2). The peaks marked with an asterisk may be due to **2b-Cr**.

preferred to one where the isocyanide ligand is bound to the acceptor metal atom. This might be expected given that the Bu^tNC is a better donor ligand than CO .^{29,30} It is interesting that reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ with $[(\mu\text{-Cl})\text{Rh}(\text{PR}'_3)_2]_2$ ($\text{R}' = \text{OPr}^i$) gives $(\eta^5\text{-C}_5\text{Me}_5)(\text{R}'_3\text{P})(\text{OC})\text{-IrRh}(\text{CO})(\text{PR}'_3)(\text{Cl})$ that contains an unbridged Ir-Rh dative bond and where there has been a migration of a PR'_3 ligand to the donor metal atom accompanied by migration of a carbonyl to the acceptor metal atom.³¹

$(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) Complexes. These complexes were prepared by the method used for the monoisocyanide derivatives except that $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ replaced $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ (i.e., eq 3, $x = 2$).

If it is assumed that the isocyanide ligands remain attached to the osmium atom in the products, then there are three possible isomers of formula $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$; these are shown as **a-c** with $\text{L} = \text{Bu}^t\text{NC}$ (this, of



course, also assumes that there are no bridging ligands and each metal has approximate octahedral coordination). The ^{13}C NMR spectra of the products formed initially in the reaction (**2a-M**) have, besides the typical pattern for the $\text{M}(\text{CO})_5$ unit, a 2/1 pattern in the region associated with resonances of carbonyls bound to osmium (see Table III). Furthermore, the signal of intensity 1 appears at high field that is taken to be characteristic of a carbonyl ligand trans to a dative metal-metal bond. Structure **c** may therefore be ruled out, in agreement with previous results discussed above. The ^{13}C NMR spectra are, however, consistent with

(25) $\text{Mn}_2(\text{CO})_{10-x}(\text{PR}_3)_x$ complexes: (a) Giordano, R.; Sappa, E.; Tiripicchio, A.; Tiripicchio Camellini, M.; Mays, M. J.; Brown, M. P. *Polyhedron* 1989, 8, 1855. (b) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Vol. 4 p 11 and references therein. $\text{Re}_2(\text{CO})_{10-x}(\text{PR}_3)_x$ complexes: Boag, N. M.; Kesz, H. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Vol. 4 p 171 and references therein.

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(27) (a) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1978, B34, 666. (b) Alex, R. F.; Einstein, F. W. B.; Jones, R. H.; Pomeroy, R. K. *Inorg. Chem.* 1987, 26, 3175. See also: (a) Venäläinen, T.; Pakkanen, T. *J. Organomet. Chem.* 1984, 266, 269. (b) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1988, 347, 157.

(28) Mays, M. J.; Gavins, P. D. *J. Chem. Soc., Dalton Trans.* 1980, 911. See also: (a) Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1983, 2365. (b) Ma, A. K.; Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *Organometallics* 1990, 9, 45.

(29) Treichel, P. M. *Adv. Organomet. Chem.* 1973, 11, 21.

(30) (a) Yamamoto, Y. *Coord. Chem. Rev.* 1980, 32, 193. (b) Harvey, P. D.; Butler, I. S.; Harris, G. W.; Coville, N. J. *Inorg. Chem.* 1986, 25, 3608.

(31) Del Paggio, A. A.; Muetterties, E. L.; Heinekey, D. M.; Day, V. W.; Day, C. S. *Organometallics* 1986, 5, 575.

either structure **a** or **b** for the initial products. The infrared spectra (e.g., Figure 4A) in the region 2150–2250 cm^{-1} exhibited only one NC stretching absorption, which is consistent with **a** for the structure of the initial products. This might have been the expected structure given the diaxial arrangement of the isocyanide substituents in the starting complex $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$.

When the **2a-M** complexes were stirred in hexane at room temperature for 7–10 days, they rearranged to a second isomer (**2b-M**), which precipitated from solution. Because the **2b-M** products were much less soluble in hexane than the **2a-M** isomers, they could be obtained pure by recrystallization from CH_2Cl_2 /hexane.

The ^{13}C NMR spectra of the **2b-M** complexes are similar to those of the corresponding **2a-M** complexes (Table III). In particular, the spectrum of each **2b-M** compound has a resonance of intensity 1, in the 170–165 ppm region, consistent with a carbonyl trans to a dative metal–metal bond. Furthermore, the **2b-M** isomers exhibit two infrared-active NC stretches (Table II; see also Figure 4B). The spectroscopic properties of these complexes are therefore consistent with structure **b** with the isocyanide ligands cis to one another and also cis to the Os–M bond. (The pattern of the carbonyl stretches in the 1975–2100- cm^{-1} region of the infrared spectra of the **2b-M** complexes is also consistent with a *fac*- $\text{Os}(\text{CO})_3(\text{X})_2(\text{Y})$ arrangement of ligands.)

Configuration **b** might be expected to be favored over configuration **a** for electronic reasons since in **b** all the carbonyl ligands are trans to poor π -acceptor ligands. In $\text{Re}_2(\text{CO})_6(\text{CNC}_6\text{H}_5\text{Me}_2)_4$ each rhenium atom has two equatorial isocyanide ligands that are also mutually cis.²⁶ The difference in the stability of the **2b-M** and **2a-M** isomers must, however, be small. This is because when the pure **2b-M** complexes were stirred in CH_2Cl_2 at room temperature ($\sim 25^\circ\text{C}$), they isomerize over 2–10 days to give an equilibrium mixture that contained significant concentrations of the corresponding **2a-M** isomer. It was verified for the chromium and molybdenum derivatives that equilibrium could be attained under the same conditions starting from predominantly the **a** isomer. The approximate **a/b** isomer ratios as determined by ^1H NMR spectroscopy were 1/2.6, 1/1.8, and 1/2.3 for **2-Cr**, **2-Mo**, and **2-W**, respectively.

The mechanism of the isomerization has not been studied. If, however, the formation of the complexes involves the reaction of $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ with the intermediate $\text{M}(\text{CO})_5$ (derived from $\text{M}(\text{CO})_5(\text{THF})$), then by the principle of microscopic reversibility the isomerization cannot involve the dissociation of $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ into these two species. If the isocyanide ligands remain on osmium, as appears probable, the isomerization also cannot proceed via an intermediate with two bridging carbonyls as is thought to occur in the $(\text{R}_3\text{P})(\text{OC})_4\text{OsM}(\text{CO})_5$ complexes.⁴ A mechanism that does account for the isomerization is a trigonal twist at the osmium atom that takes a *mer*- $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2[\text{M}(\text{CO})_5]$ configuration to the *fac* isomer via a trigonal-prismatic intermediate. Trigonal-twist mechanisms have been proposed before to account for nondissociative isomerizations of metal carbonyl compounds.³²

The structure of **2b-Cr** was confirmed by X-ray crystallography. A view of the molecule is given in Figure 5;

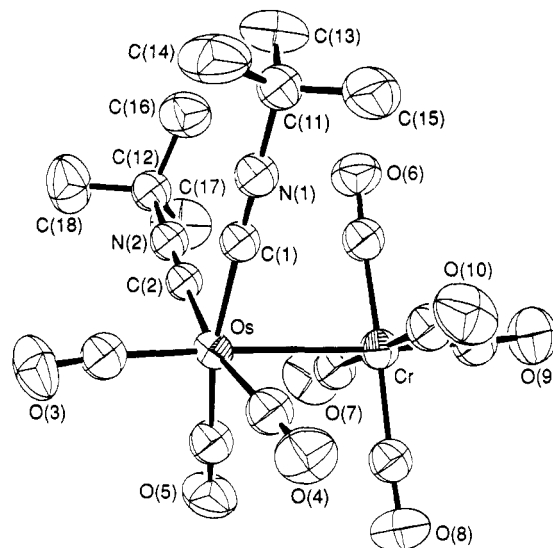


Figure 5. Molecular structure of $[\text{cis-dieq}-(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{Os}]-\text{Cr}(\text{CO})_5$ (**2b-Cr**).

bond length and angle data are given in Table VIII. In a similar manner to **1-Cr**, the 18-electron compound $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ acts as a 2-electron donor ligand to the chromium atom via an unbridged dative metal–metal bond. The comparable bond lengths in **2b-Cr** and **1-Cr** are equal within error. For example, the Os–Cr bond length in **2b-Cr** is 2.9693 (12) Å whereas in **1-Cr** it is 2.966 (2) Å. As found for **1-Cr**, the equatorial carbonyls on the osmium atom lean toward the chromium atom (the $\text{OC}_{\text{eq}}-\text{Os}-\text{Cr}$ angles are approximately 80°). The isocyanide ligands do not lean inward (the appropriate C–Os–Cr angles are approximately 88°).

The results for the $(\text{OC})_3(\text{Bu}^t\text{NC})_2\text{OsM}(\text{CO})_5$ complexes are in contrast to our unpublished results for $(\text{OC})_3(\text{Me}_3\text{P})_2\text{OsW}(\text{CO})_5$ (**4**).³³ In CH_2Cl_2 solution **4** exists as a mixture of isomers **a** and **c** ($\text{L} = \text{PMe}_3$) in an approximate 1/1 ratio with no evidence for isomer **b**. In the solid state, **4** has structure **c** and the Os–W bond is markedly longer than that in $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ (where the PMe_3 ligand is trans to the metal–metal bond). The long Os–W bond in **4** suggests it is weak probably due to steric interactions between the methyl groups and the equatorial carbonyls on the tungsten atom. Significantly, we have been unable to prepare the chromium or molybdenum analogues of **4**.

The stability of complexes **1-Cr** and **2-Cr** may also be compared to $(\text{OC})_5\text{OsCr}(\text{CO})_5$, which decomposes in solution at room temperature with a half-life of approximately 2 min.⁴ (We have been unable to prepare the molybdenum and tungsten congeners of $(\text{CO})_5\text{OsCr}(\text{CO})_5$.) It therefore appears that $\text{Os}(\text{CO})_4(\text{CNBu}^t)$ and $\text{Os}(\text{CO})_3(\text{CNBu}^t)_2$ are superior donor ligands to $\text{Os}(\text{CO})_5$, $\text{Os}(\text{CO})_4(\text{PMe}_3)$ or $\text{Os}(\text{CO})_3(\text{PMe}_3)_2$. It is generally accepted that isocyanide ligands are better σ donors than the carbonyl ligand.^{29,30} Furthermore, the rodlike Bu^tNC ligand³⁴ can readily adopt a site that is cis to the metal–metal dative bond without too much steric interaction with the equatorial carbonyls on the group 6 atom. For reasons discussed above, this appears to be the site that is electronically favored by the poorer π -acceptor ligand. It is interesting that $(\text{OC})_3[\text{MeC}(\text{CH}_2\text{O})_3\text{P}]_2\text{OsOs}(\text{CO})_4\text{W}(\text{CO})_5$, which has two, un-

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bridged, dative metal-metal bonds (i.e., Os→Os→W), is a remarkably stable molecule.⁷ The X-ray structure of the compound reveals that the sterically undemanding P-(OCH₂)₃CMe ligands³⁵ occupy positions that are mutually trans but are also cis to the Os-Os dative bond.⁷ It thus appears that, for compounds of the type Os(CO)_{5-x}(L)_x (x = 1, 2) to be good donor ligands, L should be a good σ-donor ligand and small so that it can occupy a site cis to the dative metal-metal bond.

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Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We also thank Professor J. Takats (University of Alberta) for a copy of Dr. M. R. Burke's Ph.D. thesis.

Supplementary Material Available: Figures of the carbonyl region of the ¹³C NMR spectrum of 1-Cr, 1-Mo, and 1-W and the carbonyl region of the ¹³C NMR spectrum of 2a-Cr, 2a-Mo, and 2a-W, a listing of supplementary crystallographic data for 1-Cr and 2b-Cr, and tables of hydrogen atom coordinates and anisotropic temperature factors for 1-Cr and 2b-Cr (6 pages); listings of observed and calculated structure factors for 1-Cr and 2b-Cr (25 pages). Ordering information is given on any current masthead page.

Synthesis and Carbonyl Exchange in (η⁵-C₅R₅)(OC)Ir[Os(CO)₄]₂ (R = H, Me). Structure of (η⁵-C₅Me₅)(OC)Ir[Os(CO)₄]₂

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Received September 25, 1990

The clusters (η⁵-C₅R₅)(CO)Ir[Os(CO)₄]₂ (R = H, 1; R = Me, 1*) were isolated (28% yield) as air-stable, red crystals from the reaction of (η⁵-C₅R₅)Ir(CO)₂ and Os(CO)₄(η²-cyclooctene) in hexane at 55–65 °C. The structure of 1* has been determined by X-ray crystallography: space group *P*1̄ with *a* = 9.107 (3) Å, *b* = 9.128 (2) Å, *c* = 14.639 (2) Å, α = 84.63 (1)°, β = 78.96 (2)°, γ = 66.90 (2)°, *Z* = 2, *R* = 0.030, *R*_w = 0.040 for 3738 reflections (*I* ≥ 2.5σ(*I*)). The structure consists of an Ir(η⁵-C₅Me₅)(CO) and two Os(CO)₄ units bound in a triangular array (Ir–Os(1) = 2.7902 (5), Ir–Os(2) = 2.8124 (5), Os(1)–Os(2) = 2.8536 (5) Å); the carbonyl ligand bound to the iridium atom occupies an axial site. The ¹³C NMR spectrum of 1 in CH₂Cl₂/CD₂Cl₂ at -48 °C exhibits five sharp carbonyl resonances in the ratio 2:2:1:2:2 consistent with a rigid structure similar to that of 1* in the solid state. On warming the sample to +7 °C, four of the carbonyl resonances collapsed to the base line. This mode of collapse is interpreted in terms of partial merry-go-round CO exchanges that occur in the two planes that are perpendicular to the plane of the metal atoms and pass through the Ir and one of the Os atoms. Simulation of the spectrum at -10 °C indicated Δ*G*[‡] = 14.2 kcal mol⁻¹ for the barrier to the exchange. Cluster 1* exhibited similar behavior but with a much lower activation energy for the CO exchange: Δ*G*[‡] = 7.4 kcal mol⁻¹ (from the simulation of the spectrum at -116 °C).

Introduction

One of the fascinating properties of metal carbonyl clusters is the stereochemical nonrigidity they often exhibit.^{1,2} A number of different types of CO exchange have been identified, and plausible mechanisms have been proposed for these processes. It is still not clear, however, why one process has a low activation barrier whereas another, which superficially resembles the first, has a much higher barrier.

We have recently described the synthesis and structure of the triangular cluster (OC)₅Cr[Os(CO)₃(PMe₃)₂].³ The

¹³C NMR spectrum of this cluster in solution at -122 °C had carbonyl resonances that were consistent with the presence of two isomers, and in each isomer the four radial carbonyls of the Cr(CO)₅ unit were equivalent but not equivalent to the axial carbonyl. The latter observation was taken to indicate that there was rapid rotation of the Cr(CO)₅ unit about an axis that passes through the Cr atom and the midpoint of the Os₂ vector.³ At higher temperatures, the spectra of each isomer underwent changes consistent with at least two other types of carbonyl exchange. The molybdenum and tungsten analogues of (OC)₅Cr[Os(CO)₃(PMe₃)₂] behaved similarly.⁴

The triosmium cluster (OC)₄Os₃[Os(CO)₃[P(OMe)₃]]₂ also exhibits ¹³C NMR signals, in solution at -66 °C, consistent with the presence of two isomers analogous to those of (OC)₅Cr[Os(CO)₃(PMe₃)₂].⁵ The Os(CO)₄ units in each isomer are, however, rigid. Indeed, one carbonyl resonance

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