Complexes Containing Unbridged Dative Metal−Metal Bonds and the Strong Acceptor $Ru(CO)_3(SiCl_3)_2$ Moiety. Comments on the Transition Metal to Silicon Bond

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Complexes of formula $(R_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, Os) and $(OC)_3(Bu^tNC)_2MRu(CO)_3(SiCl_3)_2$ (M = Fe, Ru, Os) have been prepared from the reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ and the appropriate donor molecule in solution at room temperature. The characterization of the complexes included the crystal structures of $(Me_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, **1Ru**; Os, **1Os**) and the three $M(CO)_3(CNBu^t)_2$ derivatives (**3Fe**, **3Ru**, **3Os**). All five structures reveal molecules with unbridged metal−metal bonds. The PMe_3 ligand is trans to the metal bond in **1M**, whereas the isocyanide ligands are cis to this bond in **3M**. The Bu^tNC substituents have a cis configuration in **3Fe** and **3Ru**, but a trans arrangement in **3Os**. Complexes **3Fe**, **1Ru**, and **3Ru** are rare examples of structurally characterized compounds in which a first-row or second-row transition metal acts as the donor atom in a molecule containing an unbridged dative bond between two transition metals. The $(OC)_3(Bu^tNC)_2FeRu(CO)_3(SiCl_3)_2$ derivative is unstable both in solution and the solid state and attempts to prepare similar complexes in which Fe acts as the donor atom were unsuccessful. In contrast to previous studies, the $Ru(CO)_4(PR_3)$ derivatives were reasonably stable. The RuSi lengths trans to the dative metal−metal bond (range 2.338(3)−2.357(2) Å) are considerably shorter than the RuSi lengths trans to the carbonyl ligand (range 2.399(5)−2.420(4) Å), whereas there is no significant difference between the SiCl lengths in the two types of $SiCl_3$ ligands in the five structures. These results are interpreted in terms of the trichlorosilyl ligand acting as a π acceptor ligand principally via the Si 3d orbitals.

Introduction

In 1983 we described the synthesis and structure of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$, believed to be the first complex structurally characterized with an unbridged donor−acceptor bond between two transition metals.[1] Since that date we and others have reported further examples of complexes with unbridged dative metal−metal bonds, but they are still extremely rare.[2−8] In one study we reported the syntheses of $(R_3P)(OC)_4OsM'(CO)_5$ (M′ = Cr, Mo, W) complexes, which are air-stable crystalline solids. We were, however, unable to prepare Fe or Ru analogues of these complexes.[4a]

In preliminary studies in this laboratory, it became apparent that the 16-electron groupings $Os(CO)_3(GeCl_3)(Cl)$ and $Ru(CO)_3(SiCl_3)_2$ were superior acceptor fragments to the $M'(CO)_5$ units.[1,4,5,9] This suggested that weaker "18-electron ligands" might form stable adducts with the group 8 acceptor fragments. The $Ru(CO)_3(SiCl_3)_2$ unit was chosen in order to examine this possibility even though the preliminary evidence indicated it was a somewhat weaker acceptor fragment than the $Os(CO)_3(GeCl_3)(Cl)$ moiety. This was because the precursory complex, *cis*-$Ru(CO)_4(SiCl_3)_2$, is conveniently prepared and loses a carbonyl ligand readily in solution at room temperature and hence affords derivatives of formula *mer,cis*-$Ru(CO)_3(L)(SiCl_3)_2$ (L = two-electron donor ligand) under mild conditions.[10,11] Furthermore, it is found that when there is a halide ligand attached

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Table 1. Analytical and IR Data for $(Dnr)Ru(CO)_3(SiCl_3)_2$ Complexes

Dnr	%C(calc)	%H(calc)	ν(CO) cm^{-1} (CH_2Cl_2)
$[(MeC(CH_2O)_3P](OC)_4Ru$	17.68(17.66)	1.11(1.10)	2136 (w), 2127 (w), 2107 (w), 2084 (w, sh), 2074 (w, sh), 2062 (s), 2017 (m)
$[(MeO)_3P](OC)_4Ru$	15.30(15.17)	1.14(1.14)	2130 (w), 2071 (w, sh), 2052 (s), 2016 (m)
$(Me_3P)(OC)_4Ru$	16.38(16.16)	1.18(1.22)	2122 (w), 2068 (w, sh), 2044 (vs), 2013 (vw, sh)
$(Ph_3P)(OC)_4Ru$	32.29(32.28)	1.72(1.61)	2123 (w), 2073 (m), 2045 (s), 2017 (m)
$[(PhO)_3P](OC)_4Ru$	30.60(30.72)	1.62(1.55)	2130 (w), 2077 (m), 2057 (s), 2021 (m)
$(Cy_3P)(OC)_4Ru$	31.69(31.68)	3.46(3.48)	2116 (w), 2071 (m), 2041 (w, sh), 2037 (s), 2023 (w, sh), 2011 (w, sh)
$[(MeC(CH_2O)_3P](OC)_4Os$	16.70(16.50)	1.15(1.04)	cis:[b] 2130 (w), 2081 (w, sh), 2070 (vw, sh), 2054 (vs), 2020 (w, sh); trans: 2124 (vw), 2073 (vw, sh), 2056 (vs), 2016 (w, sh);
$(Me_3P)(OC)_4Os$	14.55(14.43)	1.10(1.09)	2124 (w), 2069 (w, sh), 2038 (vs), 2012 (vw, sh)
$(Ph_3P)(OC)_4Os$	29.37(29.48)	1.38(1.48)	2123 (w), 2073 (m), 2039 (s), 2025 (w, sh), 2015 (w, sh)
$(Bu^tNC)_2(OC)_3Fe$	25.38(25.26) 3.74(3.68)[a]	2.32(2.37)	2091 (w), 2055 (s), 2031 (vs), 1997 (w, sh); ν(CN): 2196 (m), 2176 (m)
$(Bu^tNC)_2(OC)_3Ru$	23.65(23.85) 3.55(3.48)[a]	2.24(2.24)	2093 (m), 2065 (s), 2048 (sh), 2041 (s), 2021 (w), 2006 (m); ν(CN): 2213 (m), 2194 (m)
$(Bu^tNC)_2(OC)_3Os$	21.20(21.47) 2.90(3.13)[a]	2.17(2.03)	2098 (w), 2062 (m), 2036 (s), 2022 (w, sh), 2004 (m); ν(CN): 2222 (w), 2193 (s)

[a] %N(calc). [b] See text.

to the acceptor moiety, there is a tendency for this ligand to migrate to the donor half of the adduct with concomitant migration of a carbonyl ligand to the acceptor metal atom.[5,6,9a] The resulting isomer of the original complex has a nondative metal−metal bond (cf. the isomers $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)(Br)$, with a dative OsRu bond, and $(Me_3P)(OC)_3(Br)OsRu(CO)_4(SiCl_3)$ with a nondative OsRu bond).[5] The trichlorosilyl ligand does not show this migratory tendency.[5]

Herein, we report the synthesis and structures of a number of derivatives of the type $(Dnr)Ru(CO)_3(SiCl_3)_2$, where Dnr is an 18-electron carbonyl complex of a group 8 metal and includes several stable complexes in which ruthenium acts as the donor atom. The crystal structure of one complex that has iron as the donor atom is also described. Furthermore, the Ru−Si and Si−Cl lengths in the structures, we believe, provide important insights into the nature of the transition metal to silicon 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. Hydrocarbon solvents were refluxed over potassium, distilled, and stored over molecular sieves before use. Dichloromethane was dried in a similar manner except that P_2O_5 or CaH_2 was employed as the drying agent. The precursory complex, *cis*-$Ru(CO)_4(SiCl_3)_2$, was prepared by a literature procedure and was sublimed before use.[11] Compounds of the type $Ru(CO)_4(PR_3)$ were prepared in excellent yield from $Ru(CO)_5$ and PR_3 in hexane at room temperature.[12,13] The solution IR spectra (CO stretching region) of the compounds agreed with those reported in the literature. The preparation of $Os(CO)_4(PR_3)$ compounds also followed literature procedures.[4a,12,13b] The preparation of $Fe(CO)_3(CNBu^t)_2$ and $Os(CO)_3(CNBu^t)_2$ has also been previously reported;[14,15] the syntheses of $Ru(CO)_3(CNBu^t)_2$ and an alternative preparation of the Fe analogue are presented herein. With the exception of $(OC)_3(Bu^tNC)_2FeRu(CO)_3(SiCl_3)_2$, the preparation of the new complexes followed the same general procedure; two representative syntheses are described below along with that of the Fe compound. Yields ranged from ∼20% (for $(OC)_3(Bu^tNC)_2OsRu(CO)_3(SiCl_3)_2$) to ∼80% (for $(Me_3P)(OC)_4RuRu(CO)_3(SiCl_3)_2$).

Analytical and spectroscopic data for the new compounds are given in Tables 1 and 2, respectively (NMR spectra were recorded on a Bruker AMX400 spectrometer). The EI mass spectra of several of the new compounds were determined, but gave ions at highest *m*/*z* corresponding to $[Ru(CO)_3(SiCl_3)_2]^+$ and ions due to donor unit (i.e., the parent ions were not observed).

Preparation of $Fe(CO)_3(CNBu^t)_2$. A round-bottom flask (∼100 mL; fitted with a Teflon valve) with $Fe(CO)_5$ (0.85 g; 4.3 mmol), *tert*-butylisocyanide (1.00 mL; 0.74 g; 8.8 mmol), and hexane (35 mL) was cooled to −196 °C and evacuated; the solution was degassed with three freeze−pump−thaw cycles. The vessel was sealed under vacuum and heated at 110 °C for 14 h. During this period the flask was cooled to −196 °C and evacuated, and the solution degassed as previously described. The vessel was cooled to room temperature, and the solution transferred to a Schlenk tube, which was then stored at −25 °C overnight; the desired product, $Fe(CO)_3(CNBu^t)_2$, was obtained (0.82 g; 62%) as spectroscopically pure, yellow crystals: IR (hexane) ν(CN) 2115 (m), 2081 (w); ν(CO) 1997 (w), 1955 (vw), 1933 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49 (C_6D_6) δ 0.89. Lit.:[14] IR ($CHCl_3$) ν(CN) 2130; ν(CO) 1998, 1922 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.92.

Preparation of $Ru(CO)_3(CNBu^t)_2$. A bomb (200 mL; Parr Instrument Co.) was charged with $Ru_3(CO)_{12}$ (0.480 g, 0.751 mmol) and hexane (60 mL) and pressurized with CO (100 atm). The vessel and contents were heated at 140 °C for 15 h. The vessel was cooled to room temperature, and the solution was transferred to a Schlenk tube and placed in dry ice for 1 h. The resulting pale yellow solution of $Ru(CO)_5$ was transferred to a second Schlenk tube. The remaining solid was unreacted $Ru_3(CO)_{12}$ (0.187 g). A portion of the solution of $Ru(CO)_5$ (48 mL) was place in a bomb (200 mL), and *tert*-butylisocyanide (0.25 mL; 0.185 g; 2.23 mmol) added. The bomb was sealed, flushed three times with CO, pressurized with CO (40 atm), and heated at 110 °C for 17 h. After this period, the bomb was cooled to room temperature, gases were vented, and the solution was transferred to a Schlenk tube, which was then stored at −20 °C for 3 days, whereupon the desired product, $Ru(CO)_3(CNBu^t)_2$, was obtained (0.29 g; ∼87%) as spectroscopically pure, pale yellow crystals: IR (hexane) ν(CN) 2134 (m), 2077.5 (w); ν(CO) 2010 (vw), 1997 (vvw), 1935.5 (vs) cm^{-1}; MS, *m*/*e* 352 (vw, P$^+$), 324 ([P − CO]$^+$); ^{1}H NMR (C_6D_6) δ 0.85 (unstable in $CDCl_3$).

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Table 2. NMR Data for (Dnr)Ru(CO)$_3$(SiCl$_3$)$_2$ Complexes[a]

			^{13}C NMR δ (CH$_2$Cl$_2$/CD$_2$Cl$_2$); CO region	
Dnr	^{1}H NMR δ	^{31}P{^{1}H} NMR δ	Dnr	Ru(CO)$_3$(SiCl$_3$)$_2$
[(MeC(CH$_2$O)$_3$P](OC)$_4$Ru[b]	0.89, 4.42(5.0),[c] 0.94, 4.48(4.9)[d]	125.4[c] 112.9[d]		
[(MeO)$_3$P](OC)$_4$Ru	3.93	121.9		
(Me$_3$P)(OC)$_4$Ru	1.95(10.5)	−49.9	20.9(30.2), 199.0(4C)	197.1(1C), 199.0(2C)
(Ph$_3$P)(OC)$_4$Ru	7.44−7.52(m), 7.57−7.67(m)	24.3		
[(PhO)$_3$P](OC)$_4$Ru	7.26−7.54(m)	121.0		
(Cy$_3$P)(OC)$_4$Ru	1.25−2.30 (m)	48.3		
[(MeC(CH$_2$O)$_3$P](OC)$_4$Os[b]	0.87, 4.44(5.0)[c]	31.3[c]	161.8(1C, 12.0), 174.6(1C, 120.7), 178.1(2C, 17.1)[c]	195.3(1C), 197.3(2C)[c]
	0.93, 4.50(5.1)[d]	32.9[d]	177.4(4C, 8.3)[d]	196.1(1C), 197.9(2C)[d]
(Me$_3$P)(OC)$_4$Os	2.16(10.7)	−52.0	181.9(4C)	196.4(1C), 198.3(2C)
(Ph$_3$P)(OC)$_4$Os		−4.4		
(Bu^{t}NC)$_2$(OC)$_3$Fe	1.52			
(Bu^{t}NC)$_2$(OC)$_3$Ru	1.53			
(Bu^{t}NC)$_2$(OC)$_3$Os	1.51			

[a] In CD$_2$Cl$_2$ or CH$_2$Cl$_2$/CD$_2$Cl$_2$ (4:1); ^{31}P coupling in parentheses. [b] Isomers present, see text. [c] Cis isomer **2c**. [d] Trans isomer **2t**.

Preparation of [MeC(CH$_2$O)$_3$P](OC)$_4$RuRu(CO)$_3$(SiCl$_3$)$_2$. A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (27 mg; 0.056 mmol) and Ru(CO)$_4$[P(OCH$_2$)$_3$CMe] (23 mg; 0.064 mmol) in hexane (15 mL) was stirred at room temperature until an IR spectrum of the solution (CO stretching region) indicated the reaction was complete (approximately 8 h). During this period a pale yellow precipitate formed. The yellow supernatant solution was removed and the precipitate washed with hexane (4 × 8 mL) and dried on the vacuum line to give the crude product (38 mg). The crude product was recrystallized from CH$_2$Cl$_2$−hexane to give [MeC(CH$_2$O)$_3$P](OC)$_4$RuRu(CO)$_3$(SiCl$_3$)$_2$ (27 mg; 59%) as pale yellow crystals.

Preparation of (OC)$_3$(Bu^{t}NC)$_2$RuRu(CO)$_3$(SiCl$_3$)$_2$. A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (120 mg; 0.248 mmol) and Ru(CO)$_3$(CNBu^t)$_2$ (71 mg; 0.20 mmol) in hexane (20 mL) was stirred at room temperature; the solution became turbid almost immediately. After 4 h the supernatant solution was removed, and the yellow precipitate washed with hexane (3 × 10 mL). The remaining solid was recrystallized from CH$_2$Cl$_2$−hexane at −25 °C to afford (OC)$_3$(Bu^{t}NC)$_2$RuRu(CO)$_3$(SiCl$_3$)$_2$ (52 mg, 32%) as pale yellow crystals.

Preparation of (OC)$_3$(Bu^{t}NC)$_2$FeRu(CO)$_3$(SiCl$_3$)$_2$. A solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (216 mg; 0.448 mmol) and Fe(CO)$_3$(CNBu^t)$_2$ (110 mg; 0.359 mmol) in hexane (80 mL) was stored without stirring at −27 °C for 2 weeks. A small quantity of orange precipitate that had formed at this stage was removed by filtration, and the filtrate stored at 10 °C for 1 week, whereupon the desired product, (OC)$_3$(Bu^{t}NC)$_2$Fe−Ru(CO)$_3$(SiCl$_3$)$_2$ (170 mg, 62%), was obtained as analytically pure yellow crystals.

Table 3. Crystal Structure Data for (Me$_3$P)(OC)$_4$MRu(CO)$_3$(SiCl$_3$)$_2$ (M = Ru, 1Ru; M = Os, 1Os)

	1Ru	**1Os**
empirical formula	C$_{10}$H$_9$Cl$_6$O$_7$PRu$_2$Si$_2$	C$_{10}$H$_9$Cl$_6$O$_7$OsPRuSi$_2$
color	pale yellow	colorless
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
a (Å)	12.3965(13)	12.4036(14)
b (Å)	15.8154(16)	15.7802(15)
c (Å)	13.1860(15)	13.1866(13)
β (deg)	100.624(9)	100.888(8)
V (Å^3), Z	2540.9(9), 2	2534.6(5), 2
D(calcd) (Mg m^{-3})	1.94	2.18
abs coeff (mm^{-1})	1.985	10.849
indpdt reflcns	3636 ($I_0 \geq 2.5\sigma(I_0)$)	4191 ($I_0 \geq 2.5\sigma(I_0)$)
R_F[a]	0.034	0.032
R_{wF}[b]	0.039	0.030

[a] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. [b] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o{}^2)]^{1/2}$. $w = [\sigma^2(F_o)^2 + kF_o{}^2]^{-1}$.

X-ray Analyses. (Me$_3$P)(OC)$_4$MRu(CO)$_3$(SiCl$_3$)$_2$ (M = Ru, 1Ru; M = Os, 1Os). The structures of **1Ru** and **1Os** were determined at Simon Fraser University. The procedure used in each case was similar and will only be described for **1Ru** (**1Ru** and **1Os** are isostructural). A pale yellow crystal of **1Ru** was mounted in a glass capillary. Data were recorded with an Enraf Nonius CAD4F diffractometer with graphite-monochromated Mo Kα radiation. Unit cell dimensions were determined from 25 well-centered reflections (40° ≤ 2θ ≤ 45°). Two standard reflections were measured every hour of exposure time and showed only small fluctuations in intensity during the course of the measurements. The data were corrected for absorption by the Gaussian integration method, and corrections were carefully checked against measured ψ-scans. Data reduction also included corrections for Lorentz and polarization effects. Crystallographic details are summarized in Table 3. The structure was solved by direct methods. After the non-hydrogen atoms were located and refined with isotropic thermal parameters, an electron density difference map showed peaks consistent with anisotropic thermal motion of most atoms as well as the locations of many of the hydrogen atoms. Anisotropic thermal parameters were included in the refinement for those atoms for which there was evidence it was appropriate. Hydrogen atoms were included in calculated positions (C−H 0.95 Å) and recalculated periodically in the early stages. In the final cycles of refinement the coordinate shifts were linked with those of the carbon atoms to which they were bound. The programs used for absorption corrections, data reduction, structure solution, preliminary refinement, and plot generation were from the NRCVAX Crystal Structure System.[16] Refinement was made using CRYSTALS.[17] Complex scattering factors for neutral atoms were used in the calculation of structure factors.[18] Computations were carried out on 80486 and pentium computers.

(OC)$_3$(Bu^{t}NC)$_2$MRu(CO)$_3$(SiCl$_3$)$_2$ (M = Fe, 3Fe; M = Ru, 3Ru; M = Os, 3Os). The structures were determined at St. Mary's University. The data were collected at −80 °C on a Siemens SMART/CCD diffractometer equipped with an LT-II low-temperature device. Diffraction data were corrected for absorption with the SADABS program. The program SHELXTL was used for the solutions of the structures and their refinements, which were based on F^2.[19]

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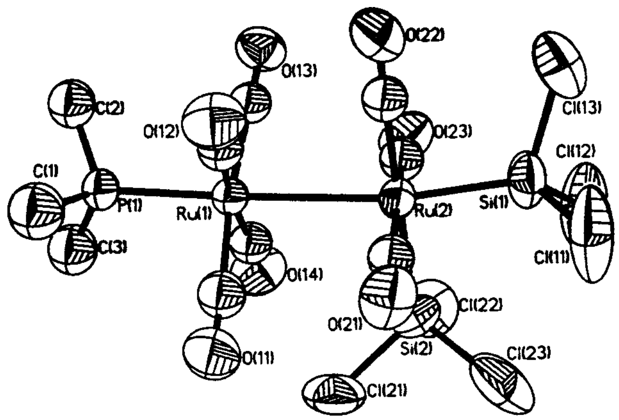

Figure 1. Molecular structure of $(Me_3P)(OC)_4RuRu(CO)_3(SiCl_3)_2$ (**1Ru**). Compound **1Os**, $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)_2$, is isostructural with **1Ru**.

Results and Discussion

$(R_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, Os) Derivatives. These derivatives were isolated (in moderate to good yield) from the reaction of *cis*-$Ru(CO)_4(SiCl_3)_2$ and $M(CO)_4(PR_3)$ in hexane at room temperature (eq 1). Derivatives of the type $Ru(CO)_2(PR_3)_2(SiCl_3)_2$ can

$$M(CO)_4(PR_3) + cis\text{-}Ru(CO)_4(SiCl_3)_2 \rightarrow (R_3P)(OC)_4MRu(CO)_3(SiCl_3)_2 \quad (1)$$

M = Ru, Os; **1Ru**: M = Ru, R = Me;
1Os: M = Os, R = Me

only be prepared from *cis*-$Ru(CO)_4(SiCl_3)_2$ if the PR_3 ligand has a small cone angle.[11,20] It was therefore not surprising that attempts to prepare bissubstituted complexes of the type $[(R_3P)(OC)_4M]_2Ru(CO)_2(SiCl_3)_2$ were unsuccessful. Furthermore, stirring $(Me_3P)(OC)_4OsRu(CO)_3(SiCl_3)_2$ in solution in the absence of $Os(CO)_4(PMe_3)$ at room temperature resulted in slow decomposition; that is, loss of the second labile carbonyl in the original *cis*-$Ru(CO)_4(SiCl_3)_2$ did not result in a characterizable compound. There was no reaction when *cis*-$Ru(CO)_4(SiCl_3)_2$ and $Fe(CO)_4(L)$ (L = PMe_3, $P(OCH_2)_3CMe$, $CNBu^t$) were stirred together in hexane at room temperature.

Structures of $(Me_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, 1Ru; M = Os, 1Os). The two compounds **1Ru** and **1Os** are isostructural with two independent molecules in the unit cell; a view of one of the molecules of **1Ru** is shown in Figure 1. Selected bond length and angle data for **1Ru** and **1Os** are given in Table 4. In each case the 18-electron compound $M(CO)_4(PMe_3)$ acts as two-electron donor ligand toward the 16-electron $Ru(CO)_3(SiCl_3)_2$ moiety via an unbridged dative metal−metal bond. Compound **1Ru** is a rare example of a complex that has been structurally characterized with an unbridged donor−acceptor metal−metal bond and in which a second-row transition metal acts as the donor atom. (Usón and co-workers have described the structure of $(\eta\text{-}C_5H_5)(OC)_2RhPt(CO)(C_6F_5)_2$, with an unbridged RhPt dative bond.)[3] The MRu bonds in the two compounds have similar lengths (in **1Ru**, 2.975(1), 2.995(1) Å; in **1Os**, 2.984(1), 3.014(1) Å). These lengths may be compared to the average MM lengths in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ of 2.8515 and 2.877 Å, respectively.[21] It is found, however, that MM lengths in noncluster compounds are somewhat longer than these lengths. For example, in *all-trans*-$(Cl_3Si)[Os(CO)_4]_3(SiCl_3)$ the two Os−Os bonds are equivalent at 2.912(1) Å.[22] In the dinuclear anions $[M_2(CO)_8]^{2-}$ the (unbridged) metal−metal vectors are 2.936(1) Å for M = Ru and 2.985(1) and 2.992(1) Å for the Os anion.[23] The dative MRu lengths in **1M** are therefore considerably longer than most comparable nondative MM lengths. This is in contrast to what is observed in the isomers $(Br)(Me_3P)(OC)_3OsRe(CO)_5$ and $(Me_3P)(OC)_4OsRe(CO)_4(Br)$, where the dative OsRe bond in the latter compound is only marginally longer than the corresponding nondative bond in the other complex.[6] The MP lengths (range 2.334(4)−2.381(4) Å) in **1M** are comparable to the OsP lengths that we have found in complexes that contain $Os(CO)_x(PMe_3)$ (x = 4, 3, 2) groupings.[4,7a,24] The discussion of the Ru−Si lengths in **1M** is postponed to a subsequent section of this paper.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(Me_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, 1aRu, 1bRu; M = Os, 1aOs, 1bOs)

Bond Lengths

	1aRu	1bRu	1aOs	1bOs
M−Ru	2.995(1)	2.975(1)	3.014(1)	2.984(1)
M−P	2.370(3)	2.376(3)	2.344(4)	2.381(4)
Ru−Si(1,3)	2.338(3)	2.342(3)	2.338(5)	2.349(4)
Ru−Si(2,4)	2.420(4)	2.413(4)	2.399(5)	2.413(5)

	range	range
M−C	1.92(1)−1.97(1)	1.92(2)−1.96(2)
Ru(2,4)−C	1.91(1)−2.01(1)	1.89(1)−1.97(2)
Si(1,3)−Cl	2.038(5)−2.088(6)	2.000(6)−2.116(8)
Si(2,4)−Cl	2.040(5)−2.082(5)	2.049(7)−2.107(7)

Bond Angles

	1aRu	1bRu	1aOs	1bOs
P−M−Ru(2,4)	176.64(8)	176.81(8)	176.8(1)	177.0(1)
M−Ru(2,4)−Si(1,3)	170.6(1)	169.6(1)	170.6(1)	170.4(1)
M−Ru(2,4)−Si(2,4)	98.51(9)	99.31(8)	98.3(1)	99.3(1)
Si−Ru(2,4)−Si	90.8(1)	91.0(1)	91.1(2)	90.2(2)

	range	range
Ru−Si(1,3)−Cl	113.4(2)−119.2(2)	114.4(3)−119.2(2)
Ru−Si(2,4)−Cl	116.2(2)−118.8(2)	116.3(2)−118.9(2)
Cl−Si(1,3)−Cl	98.3(3)−105.6(2)	97.8(3)−106.0(3)
Cl−Si(2,4)−Cl	98.6(2)−102.3(3)	98.0(3)−102.9(3)

In the structures of $(Me_3P)(OC)_4OsM'(CO)_5$ (M′ = Cr, W) there is a leaning of the radial carbonyls on the osmium atom toward the group 6 metal atom;[4] this leaning is also observed in **1Ru** and **1Os**.[25a] The leaning

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[20] Chalk, K. L.; Pomeroy, R. K. *Inorg. Chem.* **1984**, *23*, 444.

[21] (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655. (b) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[22] Willis, A. C.; van Buuren, G. N.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1983**, *22*, 1162. See also: (a) Howard, J. A. K.; Kellet, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2332. (b) Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

[23] Hsu, L.-Y.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1985**, *4*, 1483.

[24] Wang, W.; Batchelor, R. J.; Einstein, F. W. B.; Lu, C.-Y.; Pomeroy, R. K. *Organometallics* **1993**, *12*, 3598.

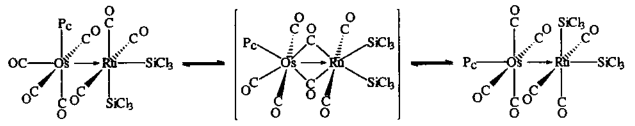
[25] (a) The shortest contact of a carbonyl carbon on the donor atom to the acceptor Ru atom in **1M** is 3.33(1) Å, an essentially nonbonding distance. (b) The range of the (nonbonded) distances from the radial C atoms (of both the CO and $CNBu^t$ ligands) on the donor atom to Ru(2) is 3.20(1)−3.42(1) Å for **3Fe**; 3.35(1)−3.50(1) Å for **3Ru**; and 3.37(1)−3.61(1) Å for **3Os**.

is somewhat less in the present compounds: the CMC angles range from 171.0(6)° to 173.1(6)° versus a range of 167.8(4)° to 169.0(3)° in the group 6 derivatives. Although the difference is small, it is consistent with the view that the $Ru(CO)_3(SiCl_3)_2$ grouping is a better acceptor than the $M'(CO)_5$ units. A stronger acceptor moiety would be expected to more fully deform the $Os(CO)_4(PMe_3)$ fragment to the ideal square pyramidal geometry it has in the complex compared with the trigonal bipyramidal geometry in the uncomplexed state. Accompanying the change in geometry would be a change in the bonding molecular orbitals on the osmium atom.

$[MeC(CH_2O)_3P](OC)_4MRu(CO)_3(SiCl_3)_2$ (2Ru, 2Os). The spectroscopic properties of all but two of the $(R_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ complexes are consistent with the presence of only one isomer in solution. The $^{13}C\{^1H\}$ NMR spectra (carbonyl region) of selected $(Me_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ complexes (Table 2) confirm that the isomer present is that with the PR_3 ligand trans to the MRu bond, as found in the solid state for **1M** (i.e., the axial isomer). The exceptions are $[MeC(CH_2O)_3P](OC)_4MRu(CO)_3(SiCl_3)_2$ (**2Ru**, **2Os**). For the osmium derivative it was found that the initially formed product (**2Os.e)** isomerized in CD_2Cl_2 at room temperature over approximately 6 h to give an equilibrium mixture containing two isomers (**2Os.a** and **2Os.e**), as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The equilibrium could also be attained by starting from pure **2Os.a** (obtained by crystallization); the ratio of **2Os.a** to **2Os.e** at equilibrium was approximately 4:1. On the basis of its ^{13}C NMR spectrum (Table 2), the minor isomer **2Os.e** is assigned a structure with the $P(OCH_2)_3CMe$ ligand cis to the Os−Ru bond (i.e., the equatorial form). Isomer **2Os.e** is the expected kinetic product since the phosphite ligand in $Os(CO)_4[P(OCH_2)_3CMe]$ is predominantly in an axial site.[12] No doubt **2Os.e** owes its existence to the small cone angle of $P(OCH_2)_3CMe$, the smallest of the PR_3 substituents used in this study.[26] When the freshly precipitated Ru analogue (i.e., **2Ru**) was dissolved in CD_2Cl_2, it gave after a few minutes ^1H and $^{31}P\{^1H\}$ NMR spectra consistent with an equilibrium mixture of isomers (Table 2). The ratio of the axial to equatorial isomers of **2Ru** was ~6:1. Attempts to detect the equatorial isomer for the PMe_3 analogue of **2Os** were unsuccessful: NMR spectra recorded as soon as possible of freshly prepared **1Os** indicated the presence of only the equatorial isomer.

To further explore the mechanism of isomerization of **2Os**, an attempt was made to prepare **2Os.e** stereospecifically labeled with ^{13}CO in the remaining carbonyl site trans to an $SiCl_3$ ligand. Addition of $Os(CO)_4[P(OCH_2)_3CMe]$ to stereospecifically ^{13}CO-labeled *cis,-cis*-$Ru(CO)_2(^{13}CO)_2(SiCl_3)_2$[10] yielded a product with the ^{13}CO scrambled over all carbonyls in the molecule. There is thus CO exchange in **2Os.e** in solution that occurs on the synthetic time scale. A mechanism that accounts for the isomerization and carbonyl exchange in **2** is the well-known terminal-bridge CO exchange shown in Chart 1.[27] However, when **1Os** was prepared from ^{13}CO-labeled $Os(CO)_4(PMe_3)$ and unlabeled *cis*-$Ru(CO)_4(SiCl_3)_2$, the ^{13}C label, as indicated by ^{13}C NMR spectroscopy, remained essentially bound to the Os atom over the time scale of the experiment.

Chart 1



2Os.e
$P_c = P(OCH_2)_3CMe$

2Os.a

$(OC)_3(Bu^tNC)_2MRu(CO)_3(SiCl_3)_2$ (M = Fe, 3Fe; M = Ru, 3Ru; M = Os, 3Os). Complexes **3M** were prepared in a fashion analogous to that used to synthesize **1M** except for the preparation of **3Fe**, where the reaction temperature employed was 10 °C and the solution was not stirred (eq 2). At this temperature **3Fe**

$$M(CO)_3(CNBu^t)_2 + cis\text{-}Ru(CO)_4(SiCl_3)_2 \rightarrow (OC)_3(Bu^tNC)_2MRu(CO)_3(SiCl_3)_2 \quad (2)$$

$$M = Fe, \mathbf{3Fe};\ M = Ru, \mathbf{3Ru},\ M = Os, \mathbf{3Os}$$

precipitated as analytically pure crystals, thus preventing its decomposition. When **3Fe** was stirred in hexane (or CH_2Cl_2) solution at room temperature, it decomposed over 16 h; two of the decomposition products were identified as $Fe(CO)_4(CNBu^t)$ and $Ru(CO)_3(CNBu^t)(SiCl_3)_2$ by IR spectroscopy.[11,14] Compound **3Fe** was also unstable in the solid state (under a nitrogen atmosphere) at room temperature.

Compounds **3Fe** and **3Ru** are isostructural; a view of **3Fe** is shown in Figure 2 and one of the two independent molecules of **3Os** in Figure 3. The dative MRu bonds in **3M**, like those in **1M**, are unbridged. Complex **3Fe** represents the first example of a neutral complex that has been structurally characterized which contains an unbridged dative metal−metal bond and where the donor atom is a first-row transition metal. Darensbourg and co-workers have described the structures of the anions $[(H)(OC)_4FeM'(CO)_5]^-$ (M′ = Cr, W) that are believed to contain unbridged FeM′ donor−acceptor bonds.[2b]

The covalent radii of Fe and Ru are given in the literature as 1.165 and 1.24 Å, respectively.[30] The FeFe distance in $[Fe_2(CO)_8]^{2-}$ is 2.792(1) Å;[31] the RuRu vector in $[Ru_2(CO)_8]^{2-}$ is 2.936(1) Å.[23] Both these values lead to a difference in the covalent radii of Fe and Ru of 0.072 Å. The FeRu distance (2.9299(7) Å) in **3Fe** is, however, only 0.019 Å shorter than the RuRu length (2.9488(2) Å) in **3Ru**. This indicates that the FeRu bond in **3Fe** is long and is consistent with the instability of the iron

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[26] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[27] As a referee has pointed out, the metal−metal bond in say $(OC)_5OsW(CO)_5$ and in $(OC)_5ReRe(CO)_5$ each consists of a pair of electrons between the metal atoms. We believe that the two bonds are, however, different since, as defined by Haaland, they differ in the nature of the chemical fragments produced when the central bond is broken.[28] We have demonstrated that upon UV photolysis, $(Me_3P)(OC)_4OsW(CO)_5$ undergoes heterolytic rather than homolytic cleavage of the OsW bond.[29] To illustrate the difference, we place an arrow between the Os and W atoms consistent with the Lewis acid−base character of the bond.

[28] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

[29] Male, J. L.; Pomeroy, R. K.; Tyler, D. R. *Organometallics* **1997**, *16* (6), 3431.

[30] Emsley, J. *The Elements*; Clarendon: Oxford, 1989.

[31] Bhattacharyya, N.; Coffy, T. J.; Quintana, W.; Salupo, T. A.; Bricker, J. C.; Shay, T. B.; Payne, M.; Shore, S. G. *Organometallics* **1990**, *9*, 2368.

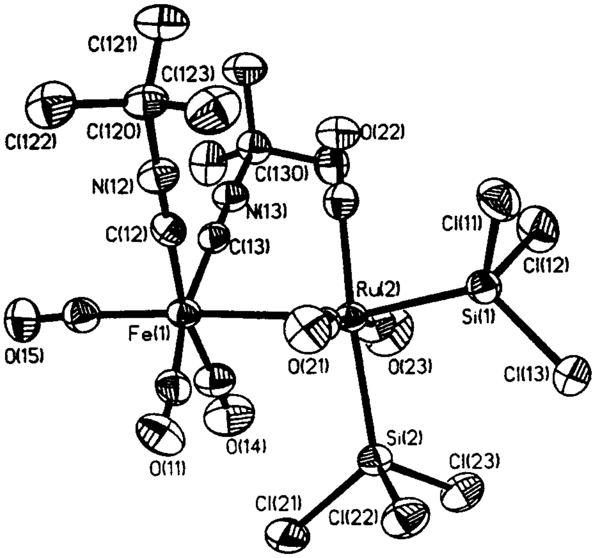

Figure 2. Molecular structure of $(OC)_3(Bu^tNC)_2FeRu(CO)_3(SiCl_3)_2$ (**3Fe**). Compound **3Ru** is isostructural with **3Fe**.

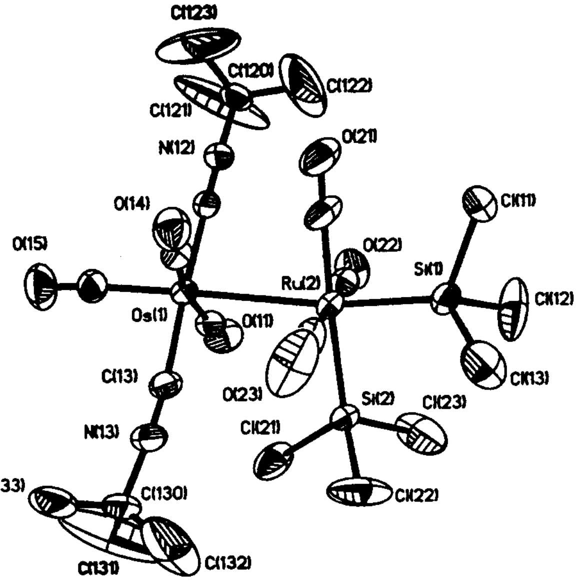

Figure 3. Molecular structure of $(OC)_3(Bu^tNC)_2OsRu(CO)_3(SiCl_3)_2$ (**3Os**).

derivative and, furthermore, that the instability may at least in part be attributed to ground-state effects. The Fe−Ru length in **3Fe** may be compared to 2.827(1) Å, the FeRu distance in $[FeRu(CO)_8]^{2-}$.[31]

The RuRu length (2.9488(2) Å) in **3Ru** is somewhat shorter than that in **1Ru** (2.975(1), 2.995(1) Å), which may indicate that $Ru(CO)_3(CNBu^t)_2$ is a slightly better donor ligand than $Ru(CO)_4(PMe_3)$ (see below). The OsRu distance in **3Os** (2.9838(6) Å) is at best, however, only marginally shorter than the corresponding vector in **1Os** (2.984(1), 3.014(1) Å).

As in **1M,** there is an inward leaning of the radial ligands attached to the donor atom in **3Fe** and **3Ru**. The $(Bu^tNC)C{-}Fe{-}CO$(radial) angles are 168.4(2)° and 170.0(2)°, whereas the corresponding angles in **3Ru** are 170.7(1)° and 171.5(1)°.[25b] Although the difference in the two molecules is barely significant, it is, for reasons discussed above, consistent with the Fe moiety as having weaker donor properties than the Ru unit. (On the basis of steric arguments, there should be less inward leaning of the equatorial ligands in the Fe derivative than in **3Ru**.) The comparable angles in $(OC)_3(Bu^tNC)_2OsCr(CO)_5$ are 166.4(3)° and 167.0(3)°.[15]

In **3Os** the isocyanide ligands are trans rather than cis with respect to each other as in **3Fe** and **3Ru**. The precursory compounds $M(CO)_3(CNBu^t)_2$ exist predominantly as the diaxial isomer in solution, as indicated by the single strong CO stretch that these compounds exhibit in the solution IR spectrum.[14,15] It is probable that the isomer with the $CNBu^t$ ligands mutually trans is initially formed and that in the case of the Fe and Ru complexes there is rapid isomerization to the form with the isocyanide ligands in a cis orientation. Attempts to detect this kinetic isomer were, however, unsuccessful. The ^1H NMR spectrum of the crude product of **3Os** in CD_2Cl_2 did exhibit weak peaks (at δ 1.58 and 1.55), one of which may have been due to the isomer analogous to **3Ru**. When pure **3Os** was stirred in toluene-d_8 for 19 h, there was no evidence for isomerization by ^1H NMR spectroscopy; heating the solution to 50 °C resulted in slow decomposition with several new resonances in the spectrum after 32 h.

It is generally accepted that $CNBu^t$ is a better σ donor but poorer π acceptor ligand than CO.[32] The thermodynamic isomer of **3M** with a fac arrangement of weak π acceptor ligands avoids two carbonyl ligands competing for the same π electron density on the metal atom. For **3Os**, the kinetic isomer (with its mer arrangement of noncarbonyl ligands) may be kinetically more stable than the corresponding Fe and Ru analogues because it has a stronger metal−metal bond compared to those in **3Fe** and **3Ru**. The equatorial/axial site preference of the isocyanide and phosphorus ligands in the **1M** and **3M** derivatives is typical for binuclear metal carbonyl complexes with these ligands.[33]

Strengths of the Dative M−Ru Bonds. Whereas $(R_3P)(OC)_4RuW(CO)_5$ complexes have at best only a fleeting existence in solution at room temperature,[4] the $(R_3P)(OC)_4RuRu(CO)_3(SiCl_3)_2$ derivatives are stable both in the solid state and in solution.[34] In a preliminary study of the strength of the metal−metal bonds in the latter complexes, **2Ru** and **2Os.e** were each separately stirred in CH_2Cl_2 with an excess of PPh_3 under a CO atmosphere at room temperature.[35] After 16 h an IR spectrum of the solution containing **2Ru** indicated approximately 50% conversion to $Ru(CO)_4(PMe_3)$ and the known compound $Ru(CO)_3(PPh_3)(SiCl_3)_2$.[11] On the other hand, there was no evidence for the formation of the latter compound (or $Os(CO)_4(PMe_3)$) in the at-

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[32] (a) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 62.

[33] (a) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1985**, *4*, 914. (b) Giordano, R.; Sappa, E.; Tiripicchio A.; Tiripicchio Camellina, M.; Mays, M. J.; Brown, M. P. *Polyhedron* **1989**, *8*, 1855. (c) 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. (d) Boag, N. M.; Kaesz, 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. (d) Harvey, P. D.; Butler, I. S.; Barreto, M. de C. W.; Coville, N. J.; Harris, G. *Inorg. Chem.* **1988**, *27*, 639.

[34] The complexes do decompose slowly in air, but this can probably be attributed to the sensitivity of the SiCl bonds to moisture.

[35] The CO atmosphere was employed in order to avoid any complications due to the lability of the remaining CO that is trans to an $SiCl_3$ group in these complexes.[20]

tempted reaction of **2Os.e** with PPh_3 after the same time, although the complex had isomerized to the equilibrium mixture of **2Os.e** and **2Os.a**. This is consistent with the view that the OsRu bond is stronger than the Ru−Ru bond in these complexes.

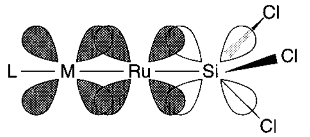
There is, however, no evidence from the MRu bond lengths in **1Ru** and **1Os** (or those in **3Ru** and **3Os**) that the bonds that involve only Ru are weaker than the corresponding OsRu bonds. Although more detailed studies are required, it may be that the increased lability of the RuOs bonds is due to transition-state stabilization rather than ground-state destabilization effects. It is well-known that complexes of second-row transition metals are more labile than their third- (and first-) row counterparts.[36]

Although several different iron complexes were tried as ligands, only in the case of $Fe(CO)_3(CNBu^t)_2$ was there evidence for complex formation, and even in this case the product (i.e., **3Fe**) was unstable in solution at room temperature. The FeRu length in **3Fe** appears long and indicates the instability of Fe−Ru dative bonds may be in part be due to ground-state effects. Certainly the evidence indicates that for this system the complexes in which Fe, a first-row transition metal, acts as the donor atom to a second-row transition metal are unstable. Complexes of the type $(R_3P)(OC)_4OsCr(CO)_5$ with Cr (a first-row transition metal atom) as the acceptor atom are however stable, but not as stable as their W congeners.[4]

In any Lewis acid−base interaction there are three factors involved in the primary interaction: the electrostatic energy of the acid−base interaction, the covalent energy of the acid−base interaction, and the energy involved when electron transfer takes place.[37] For complexes with dative metal−metal bonds the electrostatic contribution should be small because both acid and base are neutral species and the electronegativity difference between the two metal fragments is small. The covalent interaction, however, is expected to be of paramount importance. It is well-known that basicities of transition metal complexes increase on going to the complex with the metal of a chemical group lower in the periodic table.[38] It might therefore be expected that dative metal−metal bonds would be strongest for bonds with a third-row transition metal as the donor atom.[39] It would also be expected that the covalent bonding interaction would parallel that in nondative covalent metal−metal bonds. And the strength of nondative covalent bonds between two transition metals usually increases on going to metal atoms lower in the periodic table.[40]

Significant contribution to the electron-transfer energy is that required to distort the geometry of the donor molecule from what it has in the free state to that in the complex. (As pointed out above, there is a significant leaning inward of the radial ligands on the 18-electron donor molecule; that is, in the binuclear complex the donor metal atom does not have ideal octahedral coordination.) This reorganization energy is not present in the formation of a nondative covalent bond as in say $Re_2(CO)_{10}$. For this reason, dative metal−metal bonds would be expected to be weaker than comparable nondative bonds.

Chart 2



Nakatsuji and co-workers have carried out molecular orbital calculations on $(OC)_5OsM'(CO)_5$ ($M' = $ Cr, W) and $(OC)_5M''M''(CO)_5$ ($M'' = $ Mn, Re) and found that the OsCr and OsW bond lengths and force constants, although somewhat weaker, were comparable to those for MnMn and ReRe bonds.[41] The bond formation energies were, however, significantly lower for the dative metal−metal bonds and this was due to the large relaxation energy of the $Os(CO)_5$ fragment on going from the square pyramidal configuration in the complex to the trigonal bipyramidal geometry in the free state. In other words, transition-state stabilization occurs in the rupture of the dative metal−metal bond in $(OC)_5OsM'(CO)_5$ that is not present in the corresponding reaction of the homonuclear complexes. They also found that the calculated metal−metal bond formation energies for bonds that involve first-row transition metals (the MnMn and OsCr bonds) were smaller than comparable bonds with a third-row transition metal (the ReRe and OsW bonds). Despite the difference in acceptor fragments, these theoretical results are consistent with our experimental results and the qualitative arguments presented here.

Other effects, only rarely present in classical Lewis acid−base adducts, that may be important in $(L)_x(OC)_{5-x}MRu(CO)_3(SiCl_3)_2$ ($x = 1, 2$) complexes are repulsions between ligands and π interactions. In unpublished results, we have found that steric effects are important in determining the stability of $(R_3P)_2(OC)_3OsW(CO)_5$ complexes. For the complexes described here steric interactions will be greatest for the iron compounds and may contribute to their instability.

An interaction that we believe is important in these molecules (and, indeed, in molecules with nondative metal−metal bonds) is the repulsive π interaction between the filled d orbitals on the two metals; this is illustrated in Chart 2. As shown in the chart, this interaction would be decreased if good π acceptor ligands are trans to the metal−metal bond. This might account for the slightly shorter metal−metal bonds in **3Ru** and **3Os**, which have a carbonyl in one of the trans positions, compared to those in **1Ru** and **1Os**, which have PMe_3

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(36) (a) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; Wiley: New York, 1997. (b) Basolo, F. *Polyhedron* **1990**, *9*, 1503.

(37) (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; HarperCollins: New York, 1993; pp 336−341. (b) Drago, R. S.; Wong, N.; Ferris, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 1970. (c) Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953.

(38) (a) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991. (b) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.

(39) As judged by the frequencies of their CO stretches, the electron densities at the metal atoms in the three $M(CO)_4(PMe_3)$ molecules are similar and give no indication of the ligating ability of the molecules.[12]

(40) (a) Connor, J. A. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 3. (b) Johnson, B. F. G.; Roberts, Y. V. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed., Wiley: Chicester, 1994; Vol. 4, p 2177.

(41) Nakatsuji, H.; Hada, M.; Kawashima, A. *Inorg. Chem.* **1992**, *31*, 1740.

Table 5. Crystal Structure Data for $(OC)_3(Bu^tNC)_2MRu(CO)_3(SiCl_3)_2$ (M = Fe, Ru, Os; 3Fe, 3Ru, 3Os)

	3Fe	3Ru	3Os
empirical formula	$C_{16}H_{18}Cl_6FeN_2O_6RuSi_2$	$C_{16}H_{18}Cl_6N_2O_6Ru_2Si_2$	$C_{16}H_{18}Cl_6N_2O_6OsRuSi_2$
color	yellow	yellow	yellow
cryst syst	monoclinic	monoclinic	monoclinic
temp (K)	193(2)	193(2)	193(2)
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	12.5802(2)	12.6704(2)	13.4573(7)
b (Å)	14.8317(9)	14.8730(9)	17.1118(8)
c (Å)	16.2776(10)	16.1558(9)	13.7699(7)
β (deg)	91.9000(10)	92.6140(10)	107.9060(10)
V (Å^3), Z	3035.5(3), 4	3041.3(3), 4	3017.3(3), 4
D(calcd) (Mg m^{-3})	1.663	1.759	1.969
abs coeff (mm^{-1})	1.614	1.631	5.350
indpdt reflcns	6996 ($I_0 \geq 2.0\sigma(I_0)$)	7108 ($I_0 \geq 2.0\sigma(I_0)$)	7025 ($I_0 \geq 2.0\sigma(I_0)$)
R_F[a]	0.051	0.019	0.048
R_{wF}[b]	0.067	0.049	0.092

[a] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$. [b] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$. $w = [\sigma^2(F_o)^2 + kF_o^2]^{-1}$.

in this trans site. This has also been noticed in the structures of $(L)(OC)_4OsCr(CO)_5$ (L = PMe_3, $CNBu^t$).[4,15] It should be pointed out, however, that Nakatsuji and co-workers in their calculations on $(OC)_5OsM'(CO)_5$ found that the nonbonding d orbitals on Os were little affected upon complexation.[41]

The Ru–Si Bonds. There is still no general agreement as to the nature of the bonding between transition metals (M) and silicon ligands, and in particular the $SiCl_3$ ligand.[42–45] The metal–silicon bond lengths of M–$SiCl_3$ units are usually significantly shorter than the sum of the covalent radii of the metal and silicon atoms. The controversy arises as to whether this shortening can be attributed to π bonding between M and Si (and if so, the nature of the Si-based orbitals involved) or to σ-bonding effects that involve enhanced s character in the MSi bond and shortening due to ionic contributions to the bond.

The structures of **1M** and **3M** reported here, we believe, provide important insights into the nature of the M–$SiCl_3$ bond. This is because in each molecule there is a trichlorosilyl group trans to a CO ligand, a strong π acceptor ligand, and a second $SiCl_3$ unit trans to an $M(CO)_{5-x}(L)_x$ grouping, a π donor ligand (Chart 2). There is a remarkable difference in the lengths of the two types of RuSi bonds in the structures (Table 7). Whereas the RuSi bonds trans to the carbonyl ligand span the range 2.399(5)–2.420(4) Å, the corresponding bonds trans to the Ru–M bond are in the range 2.338(5)–2.357(2) Å, a difference of more than 0.05 Å. It is doubtful that such a difference can be attributed to σ-bonding effects. Such effects depend on the electronegativity difference between the M and Si atoms, but in **1M** and **3M** both $SiCl_3$ ligands are bound to the same metal atom.[46]

We believe the difference in the Ru–Si lengths is best explained on the basis of π interactions. As discussed in the previous section, the $M(CO)_4(PR_3)$ or $M(CO)_3(CNBu^t)_2$ ligands would give rise to repulsive dπ–dπ interactions between the metal d orbitals on the M and Ru atoms. This in turn would increase the π donation from the filled Ru 4d orbitals to the π acceptor orbitals on the $SiCl_3$ ligand trans to M, as shown in Chart 2 and, consequently, would result in a short RuSi bond. On the other hand, there would be little π back-bonding to the $SiCl_3$ ligand trans to CO because of the strong π acceptor properties of CO. There would therefore be less double-bond character in this Ru–Si bond which would result in a much longer bond, as observed. There is much evidence that the $SiCl_3$ ligand is a good π acceptor ligand.[42,43,47] We believe this is the reason the $Ru(CO)_3(SiCl_3)_2$ grouping is able to stabilize the metal–metal dative bond more than $M'(CO)_5$ units.

It has been suggested that like phosphorus ligands[48] silicon ligands (SiR_3) may act as π acceptors via the Si–R σ* molecular orbitals rather than the Si 3d atomic orbitals.[43,45,49] In PR_3 complexes there is an increase in the PR lengths in closely related complexes when the electron density increases at the metal center, which is consistent with this interpretation.[50] In **1M** and **3M**, however, there is no significant difference in the SiCl bond lengths in the two types of silyl ligands (Tables 4 and 6). For example, the SiCl lengths of the $SiCl_3$ unit trans to the iron atom in **3Fe** range in length from 2.069(2) to 2.083(2) Å, whereas the corresponding range for the $SiCl_3$ group in the cis position is virtually identical at 2.074(2) to 2.082(2) Å. These observations are therefore more consistent with the $SiCl_3$ unit acting as a π acceptor ligand through Si 3d orbitals rather than Si–Cl σ* molecular orbitals. The shortening of the RuSi length trans to the metal donor ligand without a concomitant increase in the SiCl lengths is also not consistent with arguments based entirely on σ bonding. The shortening of the RuSi length could be attributed to increased s character in the bond, but this would require increased p character in the SiCl bonds and hence a lengthening of the latter bonds. Although there are some significant differences in the Si–Cl lengths, especially in **1Os**, these involve SiCl bonds of the same silyl ligand and which we attribute to intra- or inter-

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(46) It is also very unlikely that the difference is due to steric effects. In **3Fe** and **3Os** the difference in the two types of Ru–Si lengths in each molecule is virtually the same (~0.07 Å) despite the much longer M–Ru length in the osmium derivative (2.984(1) versus 2.930(1) Å).

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Table 6. Selected Bond Lengths (Å) and Angles (deg) for $(OC)_3(Bu^tNC)_2MRu(CO)_3(SiCl_3)_2$ (M = Fe, Ru, Os; 3Fe, 3Ru, 3Os)

Bond Lengths

	3Fe	**3Ru**	**3Os**
M−Ru(1)	2.9299(7)	2.9488(2)	2.9838(6)
Ru−Si(1)	2.344(1)	2.3454(5)	2.357(2)
Ru−Si(2)	2.414(1)	2.4063(5)	2.420(2)
M−C(12)[a]	1.894(5)	2.028(2)	2.025(7)
M−C(13)	1.913(4)	2.035(2)	2.028(7)
	range	range	range
M−CO	1.811(5)−1.824(5)	1.941(2)−1.955(2)	1.916(8)−1.970(9)
Ru(2)−CO	1.929(5)−1.949(5)	1.925(2)−1.951(2)	1.924(8)−1.930(9)
Si(1)−Cl	2.069(2)−2.083(2)	2.079(1)−2.089(1)	2.055(3)−2.090(3)
Si(2)−Cl	2.074(2)−2.082(2)	2.075(1)−2.090(1)	2.055(3)−2.073(3)

Bond Angles

	3Fe	**3Ru**	**3Os**
M−Ru−Si(1)	166.46(3)	167.28(1)	170.82(5)
M−Ru−Si(2)	101.34(3)	100.51(1)	99.14(5)
Si(1)−Ru−Si(2)	92.10(4)	92.03(2)	89.86(7)
C(12)−M−C(13)[a]	88.9(2)	89.58(7)	177.4(3)
	range	range	range
Ru−Si(1)−Cl	112.1(1)−123.5(1)	112.1(1)−124.0(1)	114.7(1)−120.5(1)
Ru−Si(2)−Cl	114.1(1)−119.5(1)	114.6(1)−120.2(1)	115.2(1)−120.6(1)
Cl−Si(1)−Cl	101.2(1)−102.5(1)	101.0(1)−101.8(1)	98.3(2)−103.5(2)
Cl−Si(2)−Cl	100.1(1)−104.1(1)	99.5(1)−103.9(1)	99.4(2)−100.8(2)

[a] For **3Os** read C(11) for C(12).

molecular steric effects. Similarly, the Ru−Si−Cl and Cl−Si−Cl angles (Tables 4 and 6) do not show any systematic changes consistent with increased s character in the shorter Ru−Si bond, although once again, there is a significant variation in the angles within individual $SiCl_3$ ligands.

A number of $M-SiCl_3$ lengths (M = Ru, Fe) reported in the literature are collected in Table 7, along with the nature of the ligand trans to the metal−silicon bond in question.[51−55] Also included in the table are the RuGe lengths found in *cis*- and *trans*-$Ru(CO)_4(GeCl_3)_2$.[56] The lengths of the MSi bonds increase in the order (π-bound organic ring) < PPh_3 < CO, $SiCl_3$, ($GeCl_3$) for the ligand trans to the MSi bond. This order parallels the σ donor/π acceptor ability of the non-group 14 ligands and is also consistent with ECl_3 (E = Si, Ge) ligands as having exceptional π acceptor properties in these molecules.

Also included in Table 7 are some $M-SiMe_3$ lengths.[53,57] The RuSi lengths of $Ru-SiMe_3$ units are considerably longer than the corresponding bonds of $Ru-SiCl_3$ groups with similar ligands in the trans site. It is tempting to assign the shortening in the trichlo-

Table 7. Selected Ru−Si(Ge) and Fe−Si Bond Lengths

compd	M−Si length (Å)	ligand trans to Si	ref
Ru−$SiCl_3$ Compounds			
1.Ru	2.420(4), 2.413(4)	CO	*a*
1.Os	2.399(5), 2.413(5)	CO	*a*
3.Fe	2.414(1)	CO	*a*
3.Ru	2.4063(5)	CO	*a*
3.Os	2.420(2)	CO	*a*
cis-$Ru(CO)_4(GeCl_3)_2$	2.461(4)−2.478(5)[b]	CO	56
trans-$Ru(CO)_4(GeCl_3)_2$	2.477(1)[b]	$GeCl_3$	56
1.Ru	2.338(3), 2.342(3)	$Ru(CO)_4(PMe_3)$	*a*
1.Os	2.338(5), 2.349(4)	$Os(CO)_4(PMe_3)$	*a*
3.Fe	2.344(1)	$Fe(CO)_3(L)_2$[c]	*a*
3.Ru	2.3454(5)	$Ru(CO)_3(L)_2$[c]	*a*
3.Os	2.357(2)	$Os(CO)_3(L)_2$[c]	*a*
$(\eta^6-C_6H_4Bu^t_2)Ru(CO)(SiCl_3)_2$	2.338(1), 2.340(1)	η^6-arene	51
Ru−$SiMe_3$ Compounds			
$[Ru(\mu-SiMe_2)(CO)_3(SiMe_3)]_2$	2.507(8)	$SiMe_2$	57a
$Ru_2(CO)_5(SiMe_3)[(\mu-\eta^4,\eta^3-C_7H_6(SiMe_3)]$	2.452(3)	$Ru(CO)_3)[\eta^3-C_7H_6(SiMe_3)]$	57b
$Ru(CO)_2(SiMe_3)[\eta^3,\eta^2-C_8H_8(SiMe_3)]$	2.414(2)	$\eta^3-C_8H_8(SiMe_3)$	57c
$Ru_2(CO)_4(SiMe_3)[\mu-\eta^4,\eta^4,\eta^1-C_8H_8(SiMe_3)]$	2.439(2)	$Ru(CO)_2[\eta^4,\eta^1-C_8H_8(SiMe_3)]$	57d
Fe−$SiCl_3$ Compounds			
trans-$Fe(CO)_4(SiCl_3)_2$	2.326(2)	$SiCl_3$	52
mer,cis-$Fe(CO)_3(PPh_3)(SiCl_3)_2$	2.326(2)	CO	54
	2.301(2)	PPh_3	
$(\eta-C_5H_5)Fe(CO)(SiCl_3)_2(H)$	2.252(3)	$\eta-C_5H_5$	55a
$(\eta^6\text{-arene})Fe(SiCl_3)_2(H)_2$ (3)[d]	2.207(3)−2.226(2)	η^6-arene	55b
$(\eta^6\text{-arene})Fe(CO)(SiCl_3)_2$ (2)[d]	2.252(2)−2.269(2)	η^6-arene	55c
Fe−$SiMe_3$ Compound			
cis-$Fe(CO)_4(SiMe_3)_2$	2.456(2)	CO	53

[a] This work. [b] RuGe distance. [c] L = $CNBu^t$. [d] Number of structures.

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rosilyl systems as due to enhanced s character in the Ru−$SiCl_3$ bond. It could be argued, however, that the $SiMe_3$ unit has little or no π acceptor character and the difference in lengths is entirely attributable to π bonding in the Ru−$SiCl_3$ unit. What is required is a comparison of RuSi lengths involving $SiCl_3$ and $SiMe_3$ ligands when they are both trans to CO (or some other strong π acceptor ligand) so that π-bonding influences are reduced to a minimum. To our knowledge there are, however, no reported structures that contain a trans OC−Ru−$SiMe_3$ grouping.

This comparison can, nonetheless, be made employing data from structures of similar iron compounds (Table 7). The FeSi lengths in *trans*-$Fe(CO)_4(SiCl_3)_2$ and that trans to the carbonyl in *mer*,*cis*-$Fe(CO)_3(PPh_3)(SiCl_3)_2$ are identical at 2.326(2) Å. On the other hand, in *cis*-$Fe(CO)_4(SiMe_3)_2$ the Fe−Si lengths are both 2.456(2) Å, some 0.13 Å longer than the FeSi bonds in the comparable $SiCl_3$ derivatives. Although, steric and π-bonding effects in $Fe(CO)_4(SiMe_3)_2$ might be partly responsible for the increase in length, we believe that changes in σ-bonding character make the most significant contribution to the difference in the FeSi lengths. It is therefore concluded that both σ and π bonding are important in dictating the lengths of FeSi bonds.[58]

The Fe molecule Lichtenberger and Rai-Chaudhuri studied in which it was concluded that FeSi π bonding was important was $(Cp)Fe(CO)_2(SiCl_3)$, that is, trans to the π donor, Cp ligand.[42] On the other hand, the Fe molecule that Zybill and co-workers investigated and in which it was concluded there was little FeSi π bonding was *cis*/*trans*-$Fe(CO)_4(SiCl_3)_2$, that is, trans to the strong π-bonding CO or $SiCl_3$ ligands. These results are therefore reconcilable if the amount of π bonding in the FeSi bond can vary significantly with a change in the ligand environment about the Fe atom, in much the same way as that in an Fe−CO bond. (Hübler, Roper, and co-workers have independently reached a similar conclusion.[45])

Conclusions

With the strong acceptor fragment $Ru(CO)_3(SiCl_3)_2$, complexes with unbridged dative metal−metal bonds where Ru, a second-row transition metal atom, acts as the donor atom have been prepared and structurally characterized. The RuRu bond lengths are somewhat shorter than OsRu lengths in analogous complexes and suggest that RuRu and OsRu dative bonds in these complexes have comparable thermodynamic stability. Nevertheless, a preliminary study indicates that the RuRu bond in **2Ru** is more labile than the OsRu bond in **2Os** which is attributed to transition-state stabilization effects.

With the exception of **3Fe**, attempts to prepare a complex in which a compound of iron (i.e., a first-row transition metal) acts as a donor ligand to the $Ru(CO)_3$-$(SiCl_3)_2$ unit were unsuccessful. Even **3Fe** decomposed when stirred in solution at room temperature. The structure of **3Fe** reveals that the FeRu bond is long, which suggests that in this case the FeRu dative bond is intrinsically weaker than corresponding RuRu and OsRu dative bonds. Other secondary electronic and steric interactions may also contribute to the stability of dative bonds between transition metals. It appears that like nondative covalent bonds between two transition metal atoms, the bonds are strongest when they involve third-row transition metals. Dative covalent metal−metal bonds are less stable than comparable nondative covalent bonds. This may be in part due to the energy needed to distort the donor molecule from trigonal bipyramidal to square pyramidal geometry upon complex formation.

In all the structures determined here the RuSi bonds trans to the dative metal−metal bond are between 0.05 and 0.07 Å shorter than the RuSi bonds trans to a carbonyl ligand. This difference in length is rationalized by using π-bonding arguments. Back-bonding from the filled Ru 4d orbitals to Si π acceptor orbitals is significant when the $SiCl_3$ ligand is trans to the 18e organometallic moiety (presumed to be a π donor ligand) but small when it is trans to a carbonyl ligand. Like the carbonyl ligand, the $SiCl_3$ group appears to have considerable π acceptor capacity, with the amount of backbonding depending on the ligand trans to it in a metal complex. Furthermore, that the SiCl bonds do not show any significant variation in length when an $SiCl_3$ group is trans to either a strong or non π acceptor ligand is more consistent with the view that the $SiCl_3$ ligand acts as a π acceptor ligand via mainly the silicon 3d orbitals rather than the SiCl σ^* orbitals.

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Supporting Information Available: Views of **1Os** and **3Ru**; tables of crystal structure and refinement data, atomic coordinates, thermal parameters, and bond lengths and angles for compounds **1Ru**, **1Os**, **3Fe**, **3Ru**, and **3Os** (35 pages). Ordering information and Internet access instructions are given on any current masthead page.

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[58] For the Fe−$SiCl_3$ structures there is also no systematic variation in the SiCl lengths to indicate a major participation of SiCl σ^* molecular orbitals in the FeSi bonds, although as with the Ru compounds there is considerable variation in SiCl lengths within individual $SiCl_3$ ligands.