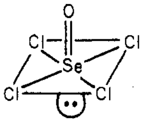
apparently coincident.

The Raman spectra of $[Et_4N]_2SeOCl_4$ and $[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$ in MeCN are very similar to each other and very different from that of the $SeOCl_3^-$ ion. This, combined with the synthetic and equilibrium evidence above, indicates the presence of a new ion, the oxotetrachloroselenate(IV) anion, $SeOCl_4^{2-}$. The expected stereochemistry for this anion is that of a square pyramid with the oxygen axial and trans to the lone electron pair:



For this C_{4v} structure, nine normal modes are expected (3 A_1 + 2 B_1 + B_2 + 3 E). The spectra in Table I show six definite bands, of which two are clearly polarized, and some low-frequency bands, which represent lattice modes but could also include low-frequency internal vibrations. The spectra are more consistent with the C_{4v} structure than with other possible structures such as a square pyramid with the oxygen cis to the lone electron pair (C_s: 8 A′ + 4 A″) or models with a stereochemically inactive lone electron pair (trigonal-bipyramid models) such as that with the oxygen equatorial (C_{2v}: 5 A_1 + A_2 + 3 B_1 + 3 B_2) and that with the oxygen axial (C_{3v}: 4 A_1 + 4 E). In the first two cases, C_s and C_{2v}, more Raman-active bands would be expected and a greater number would be polarized than are actually observed. The elimination of the C_{3v} structure on the basis of the observed spectra is less certain and rests solely on the observation of too few polarized modes in the Raman spectra. However, the C_{3v} structure with a doubly bonded oxygen at 90° to three neighboring chlorines will be a higher energy structure than the C_{2v} structure where there are only two 90° repulsions between oxygen and chlorine.

A partial assignment under C_{4v} symmetry is given in Table I. On the basis of their intensity and polarization, the bands at 944 and 242 cm^{-1} are readily assigned to ν_1 and ν_2, respectively. The third A_1 mode ν_3, is assigned at 142 cm^{-1}, which is close to the frequency of this mode in the $SeCl_5^-$ ion. Furthermore, this band, in spite of its weakness, appears to be polarized in the spectrum in Figure 1. By comparison, with the frequency of the SeO wagging mode in the spectrum of the $SeOCl_3^-$ ion (280 cm^{-1}), the band at 285 cm^{-1} is probably the comparable SeO wagging mode, $\nu_8(E)$, under C_{4v} symmetry. The remaining SeCl stretching vibrations, $\nu_4(B_1)$ and $\nu_7(E)$, are assigned at 203 cm^{-1}. These two modes lie close together in the spectrum of the $SeCl_5^-$[1] and IOF_4^-[6] ions, which also have C_{4v} symmetry and it is not unexpected that they should be coincident here. The remaining peak at 104 cm^{-1} in the spectrum of solid $[Et_4N]_2SeOCl_4$ is assigned to the symmetric in-plane $[SeCl_4]$ deformation, $\nu_6(B_2)$, which normally lies below ν_3 in the Raman spectra of comparable C_{4v} species.[6] Of the remaining modes, $\nu_5(B_1)$ and $\nu_9(E)$, the former is normally not observed for related C_{4v} species[4,6] and the latter will lie at low frequencies and it is not possible to differentiate between it and the lattice modes of $[Ph_4As]_2SeOCl_4$ and $[Et_4N]_2SeOCl_4$.

Acknowledgment. Pierre LaHaie is thanked for some preliminary work and the National Research Council of Canada is thanked for financial support.

Registry No. $bpyH_2SeOCl_4$, 27380-13-8; $[Ph_4As]_2SeOCl_4$, 71213-95-1; $[Et_4N]_2SeOCl_4$, 71213-96-2; $SeOCl_4^{2-}$, 71213-94-0.

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Halo- and Carboxylato-Bridged Binuclear Iron Carbonyls

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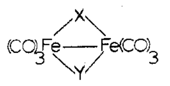
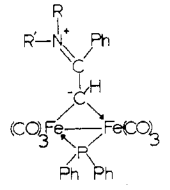
Halide and carboxylate ligands contribute three electrons and occupy two coordination sites when they are present as bridging ligands in transition-metal organometallic chemistry. We have been interested in developing synthetic routes to binuclear complexes of type **1** in which one of the groups X (X = halide or carboxylate) can be readily removed as X^- by treatment with $AgPF_6$ (X = halide) or by protonation with a strong acid such as HBF_4 (X = carboxylate) to generate binuclear cations with a vacant coordination site on each metal. To maintain the binuclear framework in such reaction sequences the Y group should be flexible but inert. In this paper we describe the synthesis of a series of binuclear iron carbonyls of type **1** in which Y is a phosphido bridge and X is a halide or carboxylate. Halo-bridged complexes of iron carbonyls are rare, the only examples known to us being the thermally unstable $Fe_2(CO)_6X_2$ (X = Br, I),[1] the methylenimino-bridged complexes $Fe_2(CO)_6(I)(N{=}CR'R'')$ (R′ = R″ = Ph, R′ = R″ = p-MeC_6H_4; R′ = Ph, R″ = t-Bu),[2] and the σ–π vinyl derivatives $Fe_2(CO)_6(X)(\mu\text{-}CH{=}CHX')$ (X = X′ = Br, I, Cl; X = Br, X′ = F; X = Br, X′ = I).[3] We describe herein the synthesis of **1** (X = Cl, Br, I, HCOO, CH_3COO, C_2H_5COO, CF_3COO; Y = PPh_2) via reaction of the organometallic zwitterions **2** (R = H; R′ = CH_3, C_2H_5) with the appropriate acid HX. The carboxylates of type **1** are the first examples of carboxylate-bridged binuclear iron carbonyls to be described.



1



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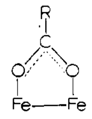

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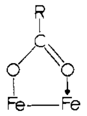

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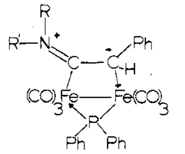

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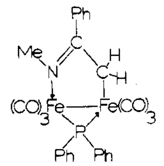

6

Experimental Section

All reactions were carried out in Schlenk tubes on a double manifold under a blanket of dry nitrogen. The starting materials of type **2** (R = H; R′ = Me, Et) were synthesized according to procedures already established for $Fe_2(CO)_6\{CHC(Ph)NHC_6H_{11}\text{-c}\}(PPh_2)$[4] and $Fe_2(CO)_6\{CHC(Ph)NEt_2\}(PPh_2)$.[5] Thus reaction of $Fe_2(CO)_6(C_2Ph)(PPh_2)$[6] (0.57 g; 1.0 mmol) with $MeNH_2$ (0.31 g; 10 mmol) or $EtNH_2$ (0.45 g; 10 mmol) in 1:1 benzene–petroleum ether between −10 and +10 °C followed by chromatography on Florisil (100–200 mesh, 18 in. × 1 in.) afforded dark red bands eluted with benzene, containing the required complexes. After recrystallization from 1:1

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Table I. Analytical Data for Halo and Carboxylate Complexes $Fe_2(CO)_6(X)(PPh_2)$ (X = Cl, Br, I, RCOO)

		% calcd				% found			
compd	mp, °C	C	H	P	X	C	H	P	X
$Fe_2(CO)_6(Cl)(PPh_2)$		43.20	2.01	6.19	7.08	42.8	2.22	6.21	6.89
$Fe_2(CO)_6(Br)(PPh_2)$		39.70	1.85	5.68	14.66	39.9	2.16	5.37	14.29
$Fe_2(CO)_6(I)(PPh_2)$		36.53	1.70	5.23	21.44	36.25	1.81	5.04	21.36
$Fe_2(CO)_6(HCOO)(PPh_2)$	105 dec	44.70	2.17	6.07		44.61	2.30	4.90	
$Fe_2(CO)_6(CH_3COO)(PPh_2)$	140 dec	45.84	2.50	5.91		45.49	2.72	5.62	
$Fe_2(CO)_6(C_2H_5COO)(PPh_2)$	125	46.88	2.81	5.75		46.71	2.90	5.60	
$Fe_2(CO)_6(CF_3COO)(PPh_2)$	140	41.56	2.23	5.36		41.36	2.23	5.10	

Table II. Spectroscopic Data for $Fe_2(CO)_6(X)(PPh_2)$

			selected IR freq, cm^{-1}			Mössbauer spectra, mm s^{-1}	
X	$\delta(^{31}P)^a$	$\delta(^1H)^b$	$\nu(CO_2)_{as}{}^c$	$\nu(CO_2)_s{}^c$	$\nu(CO)^d$	δ	Δ
HCOO	183.0	8.1–6.8 (m), 6.3 (d) (J_{P-H} = 6.0 Hz)	1567 br	1432 m	2077 s, 2036 vs, 2009 s, 1989 s, 1968 vw	0.278	1.58
CH_3COO	185.1	8.2–6.8 (m), 1.0 (s)	1548 br	1431 m	2075 s, 2034 vs, 2006 s, 1987 s, 1966 vw	0.258	1.55
C_2H_5COO		8.2–6.8 (m), 1.2 (q), 0.3 (t) (J_{H-H} = 6.0 Hz)	1540 br	1431 m	2075 s, 2034 vs, 2006 s, 1987 s, 1966 vs		
CF_3COO	183.8	8.0–6.8 (m)	1637 br	1433 m	2081 s, 2041 vs, 2014 s, 1995 s, 1974 vw	0.297	1.76
I	154.3				2069 s, 2031 vs, 2004 s, 1985 br, 1970 vs		
Br	146.0	8.0–7.0 (m)			2075 s, 2037 vs, 2008 s, 1995 m, 1987 m, 1971 w		
Cl		8.0–6.8 (m)			2077 s, 2038 vs, 2009 s, 1995 m, 1987 m, 1970 vs		

[a] Downfield (+) from 85% H_3PO_4. [b] Downfield from internal tetramethylsilane. [c] Halocarbon oil. [d] Cyclohexane.

benzene–petroleum ether, 40% and 45% yields of the methylamine and ethylamine adducts, respectively, were obtained. **$Fe_2(CO)_6${CHC(Ph)NHMe}(PPh_2)**: dark red prisms, mp 138 °C. Anal. Calcd: C, 54.30; H, 3.35; P, 5.19. Found: C, 54.15; H, 3.40; P, 5.20. IR (ν (CO), cm^{-1}; C_6H_{12}): 2038 (m), 2035 (m), 2002 (s), 1959 (s) 1954 (s), 1915 (w). **$Fe_2(CO)_6${CHC(Ph)NHEt}(PPh_2)**: dark red prisms, mp 141 °C. Anal. Calcd: C, 55.02; H, 3.63; N, 2.29. Found: C, 54.78; H, 3.72; N, 2.23. IR (ν(CO), cm^{-1}; C_6H_{12}): 2036 (m), 2034 (m), 2001 (s), 1960 (s), 1954 (s), 1914 (w).

$Fe_2(CO)_6(COOR)(PPh_2)$ (R = H, CH_3, C_2H_5, CF_3). All of these compounds were synthesized in essentially the same manner via addition of excess carboxylic acid to **2** in petroleum ether. The procedure given below for R = CH_3 is typical. To a solution of **2** (R = H, R′ = Et) (0.3 g; 0.5 mmol) in petroleum ether (20 mL) was added CH_3COOH (0.3 g; 5 mmol). An immediate color change from dark red to yellow occurred. Monitoring by IR spectroscopy indicated that the reaction was complete in 5 min as evidenced by the disappearance of ν(CO) bands due to the precursor. Evaporation to dryness and crystallization from heptane afforded a 90% yield of golden yellow **1** (X = CH_3COO). Melting point and analytical data for the carboxylates are listed in Table I. .

$Fe_2(CO)_6(X)(PPh_2)$ (X = Cl, Br). Dry HCl or HBr gas was bubbled through a benzene solution of **2** (R = H, R′ = Et) (0.5 g) (or **2** (R = H, R′ = Me)). The progress of the reaction was followed by solution IR spectroscopy; after ~30 min all of the starting complex had been consumed. Reaction solutions were reduced in volume to ~5 mL and chromatographed on Florisil with petroleum ether as eluant. The red bands afforded dark red oils on evaporation. Attempts to crystallize these oils failed. Yields of oils were in the range 60–70%. The oils can be purified by sublimation onto a cold finger (−78 °C) at 0.5 mm and 80–100 °C. The products were shown to be pure by solution IR spectroscopy in the ν(CO) region and were subsequently analyzed by high-resolution mass spectroscopy and microanalysis (Table I). **$Fe_2(CO)_6Cl(PPh_2)$**: 500 (9) M^+, 472 (45), 444 (9), 416 (4), 388 (9), 360 (25), 332 (100). $Fe_2Cl(PPh_2)^+$: obsd (^{35}Cl), 331.8931; calcd, 331.8906. **$Fe_2(CO)_6Br(PPh_2)$**: 544 (1) M^+, 516 (3), 448 (20), 432 (4), 404 (16), 376 (100). $Fe_2Br(PPh_2)^+$: obsd (^{79}Br), 375.8419; calcd, 375.8401; obsd (^{81}Br), 377.8360; calcd, 377.8381.

$Fe_2(CO)_6I(PPh_2)$. A 40% aqueous solution of HI (20 mL) and a benzene solution of **2** (R = H, R′ = Et) (0.5 g in 15 mL) were stirred vigorously at room temperature. The reaction was followed by IR spectroscopy and was complete after ~2 h. The benzene layer was removed, dried, and chromatographed as for X = Cl, Br, yielding a red oil (~70%). Mass spectrum: 592 (6) M^+, 564 (20), 536 (45), 508 (13), 480 (11), 452 (45), 424 (100) $Fe_2I(PPh_2)^+$.

Physical Measurements. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were measured in cyclohexane on a Perkin-Elmer 180 spectrometer using 0.5-mm matched sodium chloride cells. Frequencies are accurate to ±1 cm^{-1}. Phosphorus-31 and ^1H NMR spectra were obtained in C_6D_6 and $CDCl_3$, respectively, on a Bruker WP-60 FT spectrometer at field strengths of 24.29 and 60 MHz, respectively Shifts are in ppm downfield (+) of 85% H_3PO_4 and Me_4Si, respectively. Mössbauer spectra of thick pastes were measured as previously described[6] and analyzed by the least-squares fitting to Lorentzian line shapes using the program LFIT.[6] The error in the Mössbauer parameters is estimated to be ±0.01 mm s^{-1}.

Results and Discussion

Spectroscopic data for the new complexes prepared are listed in Table II. Infrared spectra in the ν(CO) region for **1** (X = HCOO, CH_3COO, C_2H_5COO, and CF_3COO) consist of four strong bands above 1985 cm^{-1} and a weaker fifth band at lower frequency. The iodide complex has a very similar spectrum, but for **1** (X = Cl, Br) the broad absorption at 1987 cm^{-1} for **1** (X = I) is resolved into a sharp doublet at 1995, 1987 cm^{-1}. The pattern of frequencies and intensities for ν(CO) closely resembles that for $Fe_2(CO)_6(OH)\{P(p\text{-}CH_3C_6H_4)_2\}$[7] ($\nu$(CO) ($C_6H_{14}$): 2081 (s), 2074 (sh), 2030 (s), 1993 (sh), 1987 (s) cm^{-1}) where $Fe(CO)_3$ groups are bridged by two different three-electron donors. Symmetrically dibridged complexes, for example $Fe_2(CO)_6(PRR')_2$,[8] also exhibit a characteristic high-frequency absorption and four or five other bands above 1955 cm^{-1}.

The value of $\nu_{as}(CO_2)$ (Table II) together with the frequency separation $\nu_{as}(CO_2) - \nu_s(CO_2)$ (135–204 cm^{-1})[9,10] suggests that the carboxylates are symmetrically coordinated as in **3** rather than unsymmetrically bound as in **4**.[11] Symmetrically bridged carboxylate ligands are well-known for metals in normal or high oxidation states but are less common for first-row transition-metal carbonyl complexes.

Mössbauer spectra of **1** ($X = RCOO$, $Y = PPh_2$) consist of a single quadrupole doublet indicating equivalence of the two iron sites. Quadrupole splittings (1.55–1.76 mm s^{-1}) are larger than values ($\leq$1.0 mm s^{-1}) associated with distorted octahedral stereochemistry,[12] and there is a marked increase in Δ on replacement of a one-carbon, three-electron bridge in **2** ($R = H$, $R' = C_6H_{11}$-c) ($\Delta = 0.65$ mm s^{-1}) by a carboxylate. We attribute this to a lengthening of the Fe–Fe bond and an increase in planarity of the $Fe_2(X)(Y)$ ring system together with a greater charge imbalance in the iron bonding orbitals generated by the presence of two cis bridging ligands (PPh_2 and RCOO) of very different electronic characteristics. Isomer shifts for **1** ($X = RCOO$, $Y = PPh_2$) are shifted toward the values for covalent Fe(II) compounds, i.e., more positive compared to those of their precursors **2**.

We have recently suggested[4] that ^{31}P NMR chemical shifts for phosphido bridges in binuclear iron carbonyls of type **1**, where the second bridging ligand X is a one-carbon, three-electron or a two-carbon, three-electron donor, are sensitive to the nature of X. Thus for example complexes of type **2** have $\delta(^{31}P; PPh_2)$ in the range of 140–160 downfield of 85% H_3PO_4 whereas in **5** where two carbon atoms are involved in bridging, $\delta(^{31}P; PPh_2)$ values lie between 180 and 190. From the wealth of X-ray data available for these derivatives[4-6,13] it is apparent that high δ values are associated with longer Fe–Fe bond lengths and larger valence angles at the bridging atom.[14] This correlation even extends to $Fe_2(CO)_6\{CH_2C(Ph)NMe\}(PPh_2)$ (**6**) ($\delta(^{31}P) = 198.5$, Fe(1)–Fe(2) = 2.704 (1) Å, Fe(1)–P–Fe(2) = 75.6 (0)°) where an $FeCH_2C(Ph)N(Me)Fe$ ring is present.[15] For the carboxylates **1**, ^{31}P shifts lie close to the value for **6** but well above the values for the halides which are much closer to the range found for type **2** compounds.[16] The structural similarity between the five-membered FeOC(R)OFe and $FeCH_2C(Ph)N(Me)Fe$ rings in **1** and **6**, respectively, is striking. On the basis of an empirical correlation of $\delta(^{31}P)$ vs. Fe–P–Fe for complexes of types **1**, **2**, **5**, and **6** we predict a bond angle of ~73° for the carboxylates **1** with an associated Fe–Fe bond length of 2.68 Å. For **1** ($X = I$) an Fe–P–Fe angle of ~70° is predicted.[17] We are currently measuring shifts for phosphido bridges in a range of binuclear iron complexes with and without metal–metal bonds in an attempt to determine whether $\delta(^{31}P)$ M–P–M bond angle correlations are structurally valid for a wider variety of complexes.

Finally we note that the facile reactions of the dipolar organometallic complexes **2** with protic acids demonstrate the not unexpected susceptibility of these molecules to electrophilic attack. In principle, electrophilic attack could occur either at the formally negative bridging carbon atom or, alternatively, on the iron–iron bond. Mechanistic studies designed to establish the intital site of attack are in progress.

Acknowledgment. We thank the National Science and Engineering Research Council of Canada for financial support.

Registry No. **1** ($X = Cl$, $Y = PPh_2$), 71000-92-5; **1** ($X = B$, $Y = PPh_2$), 71000-93-6; **1** ($X = I$, $Y = PPh_2$), 71000-94-7; **1** ($X = HCOO$, $Y = PPh_2$), 71000-95-8; **1** ($X = CH_3COO$, $Y = PPh_2$), 71031-56-6; **1** ($X = C_2H_5COO$, $Y = PPh_2$), 71000-96-9; **1** ($X = CF_3COO$, $Y = PPh_2$), 71031-57-7; **2** ($R = H$, $R' = CH_3$), 70657-55-5; **2** ($R = H$, $R' = C_2H_5$), 70657-57-7; $Fe_2(CO)_6(C_2Ph)(PPh_2)$, 52970-25-9; $MeNH_2$, 74-89-5; $EtNH_2$, 75-04-7.

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(9) The frequency separations ($\nu_{as}(CO_2) - \nu_s(CO_2)$) for **1** ($X = RCOO$) themselves do not exclusively prove symmetrical bridging since instances are known where small $\Delta\nu$ values occur for monodentate carboxylates. An example is $Ni(H_2O)_4(CH_3COO)_2$ which has $\Delta\nu = 107$ cm^{-1} and where $\nu_{as}(CO_2)$ is strongly affected by hydrogen bonding. See: (a) T. C. Downie, W. Harrison, E. S. Raper, and M. A. Hepworth, *Acta Crystallogr., Sect. B*, **27**, 706 (1971); (b) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).
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(14) For example in $Fe_2(CO)_6\{CHC(Ph)NHC_6H_{11}\text{-c}\}(PPh_2)$,[4] $\delta(^{31}P) = 158.3$, Fe(1)–Fe(2) = 2.576 (1) Å, and Fe(1)–P–Fe(2) = 70.5 (0)°, whereas for $Fe_2(CO)_6\{C(NHC_6H_{11}\text{-c})CH(Ph)\}PPh_2$,[4] $\delta(^{31}P) = 187.9$, Fe(1)–Fe(2) = 2.628 (1) Å, and Fe(1)–P–Fe(2) = 72.4 (0)°.
(15) A. J. Carty, G. N. Mott, and N. J. Taylor, unpublished results.
(16) A referee has pointed out that there are some similarities in the trends of ^{31}P chemical shifts for complexes of type **1** ($Y = PPh_2$, $X = Cl$, Br, I, RCOO) and **6** with ^{31}P shifts in phosphorus chelate complexes. Thus in compounds where the phosphido bridge is part of a six-membered ring (e.g., **1**, $Y = PPh_2$, $X = RCOO$; and **6**) shifts are 30–40 ppm downfield of values in the halide-bridged complexes where the phosphorus atom is part of a four-membered ring. For analogous chelate rings differences of 15–30 ppm are apparent. See P. E. Garrou, *Inorg. Chem.*, **14**, 1435 (1975).
(17) The chloride complex $Fe_2(CO)_6(Cl)(PPh_2)$ crystallizes on long standing. A single-crystal X-ray analysis has confirmed the molecular structure **1** ($X = Cl$, $Y = PPh_2$) with an Fe–Fe bond length of 2.560 (1) Å and an Fe–P–Fe bond angle of 69.7 (0)°.

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Dialkylbis[bis(trimethylsilyl)amido]zirconium(IV) and -hafnium(IV). Preparation and Reaction with Carbon Dioxide and *tert*-Butyl Isocyanide

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Dichlorobis[bis(trimethylsilyl)amido]zirconium(IV) and -hafnium(IV) have been prepared from the metal tetrachloride (M = Zr or Hf) and lithium bis(trimethylsilyl)amide in diethyl ether. A chloride ligand in each compound can be replaced with a tetrahydroborate group, yielding $(Cl)(BH_4)M[N(SiMe_3)_2]_2$, M = Zr or Hf. The dimethyl derivatives, $Me_2M[N(SiMe_3)_2]_2$, where M is Zr or Hf, can be prepared from the dichloro derivatives and dimethylmagnesium. Bis[(trimethylsilyl)methyl]- and diethylhafnium derivatives were similarly prepared. The hafnium dialkyls react with carbon dioxide (5–10 atm) at room temperature, yielding the carbamato derivatives $R_2Hf[O_2CN(SiMe_3)_2]_2$, where R = Me, Et, or Me_3SiCH_2. Reaction of the hafnium dialkyls (R = Me or Et) with *tert*-butyl isocyanide takes a different course, yielding $[t\text{-}BuN{=}C(R)]_2Hf[N(SiMe_3)_2]_2$, where R = Me or Et, by way of insertion into the hafnium–carbon bond. The electrophile, CO_2, inserts into the metal–nitrogen bond whereas the nucleophile, *t*-BuNC, inserts into the metal–carbon bond.