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Synthesis, Structure, and Reactivity of Stable Alkyl and Aryl Iodide Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$

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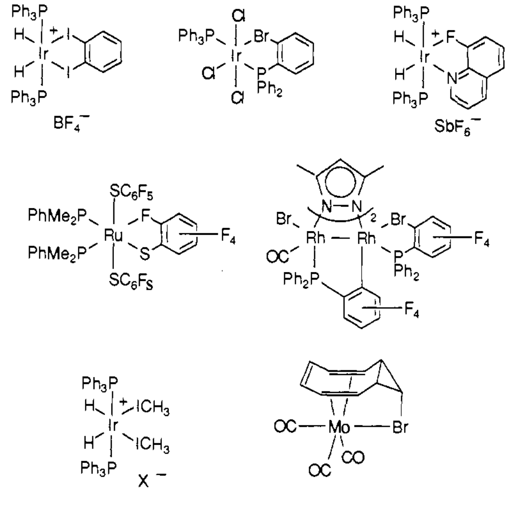
Abstract: Reaction of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ with $HBF_4{\cdot}Et_2O$ (CH_2Cl_2, −78 °C) and then alkyl and aryl iodides RI gives adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ (**3**: R = **a**, CH_3; **b**, CH_2CH_3; **c**, $CH_2CH_2CH_3$; **d**, $CH_2CH_2CH_2CH_3$; **e**, $CH_2Si(CH_3)_3$; **f**, $CH_2CH_2CH_2Cl$; **g**, CH_2Cl; **h**, C_6H_5; **i**, *p*-$C_6H_4OCH_3$; 63–87%). The structure of **3e**·$(CH_2Cl_2)_{0.5}$ is confirmed by X-ray crystallography and compared to that of iodide complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(I)$ [Re–I, 2.678 (1), 2.7210 (9) Å]. The C–I bond [2.18 (1) Å] is not significantly longer than those in free alkyl iodides. Complexes **3a–c** decompose (48–60 h, CD_2Cl_2, 25 °C) to bridging halide complexes (*SS*,*RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$ [X = I (46–65%), Cl (29–48%)] and react with CH_3CN to give acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (82–87%) and RI (72–82%). Complexes **3a–c** rapidly alkylate PPh_3 (<15 min, $CDCl_3$) to give phosphonium salts $Ph_3PR^+BF_4^-$ (93–86%) and iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (>99–92%). The reaction of **3b** and PPh_3 is second order ($\Delta H^\ddagger = 12.9 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -12.0 \pm 0.9$ eu) and $(3.3 \pm 1.3) \times 10^5$ faster (298 K) than that of ICH_2CH_3 and PPh_3 to give $Ph_3PCH_2CH_3^+I^-$ ($\Delta H^\ddagger = 16.3 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -25.9 \pm 1.5$ eu). Complex **3b** reacts similarly with Br^-, but **3h** yields IC_6H_5 and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$. Ethyl bromide and chloride complexes analogous to **3b** are less stable but can be prepared in situ.

The study of bonding between transition metals and weak Lewis bases is one of the major frontiers of inorganic and organometallic chemistry. As a result of intense recent studies, there are now numerous examples of the intramolecular coordination of unactivated sp^3 carbon-hydrogen bonds to metals,[1] as well as some cases of *inter*molecular coordination.[2] New strategies for the binding of weakly basic organic functional groups to metals should facilitate advances in molecular recognition and activation.

Alkyl and aryl halides are among the least basic heteroatomic functional groups found in organic molecules.[3] Furthermore, they undergo oxidative addition to a variety of Lewis acidic (≤16 valence electron) metal centers,[4] Accordingly, their coordination chemistry has until very recently remained unexplored.[5-11] In the early and mid-1980s, Crabtree and subsequently other researchers synthesized chelate complexes of *functionalized* aryl halides, some typical examples of which are shown in Chart I.[5,6] In 1982, Crabtree also reported the first isolable metal complex of a simple alkyl halide, $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$, and the spectroscopic detection of related species.[5] However, isolable 1:1 alkyl halide/metal adducts, which would be particularly attractive for certain types of physical studies and applications in organic synthesis, were unknown at the outset of this study.

Chart I. Representative Examples of Isolable Transition-Metal Alkyl and Aryl Halide Complexes



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(12) A complex with a chromium–$ClCH_2Cl$ distance of 3.354 Å (Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3475) has been suggested *not* to have significant chromium–chlorine bonding: Baral, S.; Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 2696.

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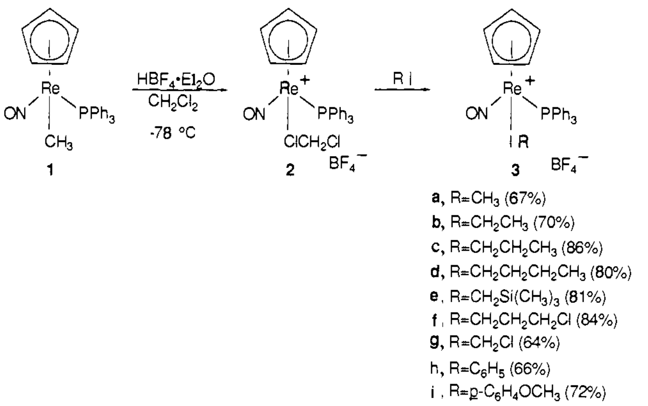
Scheme I. Synthesis of Alkyl and Aryl Iodide Complexes



We have reported that the addition of $HBF_4{\cdot}Et_2O$ to a −78 °C CH_2Cl_2 solution of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**) affords the functional equivalent of the chiral, transition-metal Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$(I).[8] When optically active methyl complex is employed, optically active Lewis base adducts are obtained with overall retention of configuration and with high optical purities.[8,13] Although the "Lewis acid" reagent decomposes above −20 °C, excellent evidence has been obtained for its formulation as the η^1-dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**).[8,9] We wondered if complexes of more basic alkyl halides (RI > RBr > RCl)[3] might have greater stability. Hence, we set out to attempt the generation of analogous chiral alkyl iodide complexes.

In this paper, we report (a) the facile synthesis and isolation of primary alkyl iodide and aryl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ (**3**), (b) physical properties of the alkyl and aryl iodide ligands, including crystal structures of an alkyl iodide complex and the related iodide complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(I)$ (**4**),[14] (c) reactions involving the alkyl and aryl iodide ligands, including quantification of the dramatic activation of the alkyl iodide ligands toward nucleophilic attack, and (d) the generation of less stable ethyl bromide and chloride complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XCH_2CH_3)]^+BF_4^-$. Selected features of these compounds will be analyzed from a theoretical viewpoint in a subsequent paper.[15] A portion of this study has been communicated.[7a]

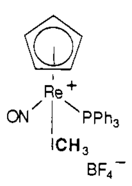
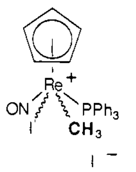
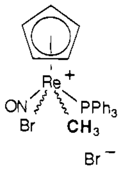
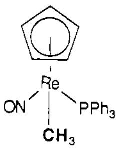
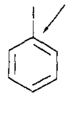
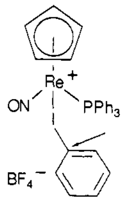
Results

1. Syntheses of Alkyl Iodide Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ (3).

Methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[16] was dissolved in CH_2Cl_2 at −78 °C and treated with $HBF_4{\cdot}Et_2O$ (0.96–1.08 equiv) to give dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**). Alkyl iodides RI [3.0–4.9 equiv; R = **a**, CH_3; **b**, CH_2CH_3; **c**, $CH_2CH_2CH_3$; **d**, $CH_2CH_2CH_2CH_3$; **e**, $CH_2Si(CH_3)_3$] were then added. Workup gave alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IR)]^+BF_4^-$ (**3a–e**) as analytically pure powders in 67–87% yields (Scheme I). Yields of **3b** and **3c** dropped somewhat when alkyl iodides were utilized in 1.2-fold excesses.

The structures of **3a–e** followed from their spectroscopic properties (Table I). The IR ν_{NO}, ^{31}P NMR chemical shifts, and ^1H and ^{13}C NMR cyclopentadienyl ligand chemical shifts were characteristic of cationic $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X'^-$ complexes. Square-pyramidal complexes of the type $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(R)(X)]^+X'^-$, which would result from carbon–halide bond oxidative addition, have been independently prepared and show cyclopentadienyl ^1H and ^{13}C NMR resonances that are much further downfield, as well as higher ν_{NO}.[8b,9,17] The ReICH protons and ReIC carbons of **3a–e** exhibited ^1H and ^{13}C NMR chemical shifts that were 0.3–0.8 and 23–24 ppm *downfield* of those in the free ligands, respectively. In contrast, the analogous ^1H NMR resonances in oxidative addition products should be *upfield* of those in the free ligands due to the shielding effect of the metal. Also, sizeable $^3J_{HP}$ and $^2J_{CP}$ would be expected.[8b,9] Some key comparisons are given in Chart II.

Chart II. Comparison of Selected ^1H and ^{13}C NMR Chemical Shift Trends

	^1H NMR (δ, CD_2Cl_2)	^{13}C NMR (ppm, CD_2Cl_2)
ICH_3	2.16	-22.7
	2.80 (s)	0.8 (d, $^3J_{CP}$= 4 Hz)
	1.60[17b] (d, $^3J_{HP}$= 11 Hz)	-1.7[17b] (d, $^2J_{CP}$= 11 Hz)
$BrCH_3$	2.71	10.0
 (two isomers)[17a]	1.50 (d, $^3J_{HP}$= 12 Hz) 2.03 (d, $^3J_{HP}$= 11 Hz)	1.0 (d, $^2J_{CP}$= 11 Hz) 10.0 (d, $^2J_{CP}$= 12 Hz)
	0.95[16] (d, $^3J_{HP}$= 5 Hz)	-37.5[16] (d, $^2J_{CP}$= 6 Hz)
	-----	94.7
	-----	130.6

The reaction sequence involving methyl iodide was monitored by ^{31}P NMR at −80 °C. When CH_3I (3.0 equiv) was added to dichloromethane complex **2** (12.90 ppm), a small new resonance attributable to methyl iodide complex **3a** appeared (12.77 ppm, ca. 5%). The probe was warmed in 10 °C increments, and the

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(13) (a) Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268. (b) Fernández, J. M.; Emerson, K.; Larsen, R. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 37. (c) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082.

(14) Crocco, G. L.; Gladysz, J. A. *Chem. Ber.* **1988**, *121*, 375.

(15) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, in press.

(16) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. The methyl ligand ^{13}C NMR chemical shift of **1** is −37.5 ppm (d, J_{CP} = 6 Hz, CD_2Cl_2), instead of −25.2 ppm (presumably a foldover artifact) as previously reported.

(17) Reactions of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and X_2 (X = Br, I; CD_2Cl_2) give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)(X)]^+X^-$ as mixtures of isomers [NMR (CD_2Cl_2, C_5H_5 ligand): δ 6.6–6.8 (^1H) and 101–104 ppm (^{13}C); see also Chart II. IR ν_{NO} 1748–1760 cm^{-1} (X = Br, KBr or CD_2Cl_2)]. Details of these labile compounds will be reported separately: (a) O'Connor, E. J., University of Utah, unpublished results; 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 12, 1986; (b) Leavitt, A.; Veal, W. R., University of Utah, unpublished results.

Table I. Spectroscopic Characterization of Alkyl and Aryl Halide Complexes

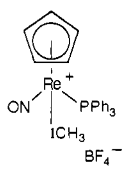
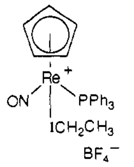
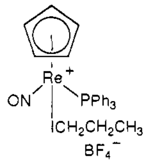
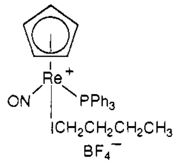
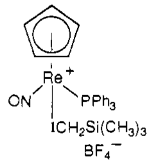
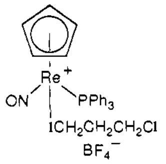
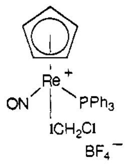
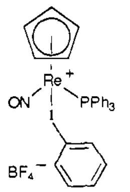
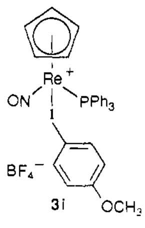
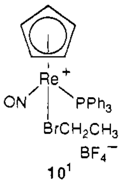
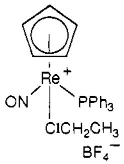
	IR,[a] $\mathrm{cm^{-1}}$	^{1}H NMR,[b] δ	^{13}C{^{1}H} NMR,[c] ppm	^{31}P{^{1}H} NMR,[d] ppm
 **3a**	ν_{NO} 1699	7.55–7.26 (m, 3 C_6H_5), 5.63 (s, C_5H_5), 2.80 (s, CH_3)	PPh_3 at 133.56 (d, J = 11.0, *o*), 132.75 (d, J = 56.0, *i*), 132.15 (d, J = 3.0, *p*), 129.63 (d, J = 11.0, *m*); 92.21 (d, J = 1.0, C_5H_5), 0.76 (d, J = 4.0, CH_3)	11.6 (s)
 **3b**	ν_{NO} 1696	7.55–7.25 (m, 3 C_6H_5), 5.62 (s, C_5H_5), 3.77 (dq, J = 9.1, 7.4, $\mathrm{IC}H\mathrm{H'}$), 3.46 (dq, J = 9.1, 7,5, $\mathrm{ICH}H'$), 1.65 (t, J = 7.4, CH_3)	PPh_3 at 133.56 (d, J = 11.0, *o*), 133.17 (d, J = 57.0, *i*), 132.08 (d, J = 2.5, *p*), 129.56 (d, J = 11.0, *m*); 92.07 (s, C_5H_5), 24.01 (d, J = 3.1, CH_2), 18.80 (s, CH_3)	11.8 (s)
 **3c**	ν_{NO} 1696	7.56–7.26 (m, 3 C_6H_5), 5.61 (s, C_5H_5), 3.75 (dt, J = 9.1, 7.2, $\mathrm{IC}H\mathrm{H'}$), 3.51 (dt, J = 9.0, 6.4, $\mathrm{ICH}H'$), 1.74 (sextet, J = 7.1, CCH_2C), 1.01 (t, J = 7.2, CH_3)	PPh_3 at 133.64 (d, J = 11.0, *o*), 132.26 (d, J = 57.3, *i*), 132.17 (d, J = 2.4, *p*), 129.64 (d, J = 11.0, *m*); 92.07 (s, C_5H_5), 34.31 (d, J = 3.0, ICH_2), 25.76 (s, $C\mathrm{H_2CH_3}$), 14.41 (s, CH_3)	11.6 (s)
 **3d**	ν_{NO} 1697	7.55–7.25 (m, 3 C_6H_5), 5.61 (s, C_5H_5), 3.76 (dt, J = 9.2, 7.4, $\mathrm{IC}H\mathrm{H'}$), 3.50 (dt, J = 9.2, 7.4, $\mathrm{ICH}H'$), 1.70 (m, $\mathrm{ICH_2C}H_2$), 1.42 (m, $\mathrm{C}H_2\mathrm{CH_3}$), 0.97 (t, J = 7.4, CH_3)	PPh_3 at 133.66 (d, J = 11.0, *o*), 133.29 (d, J = 57.4, *i*), 132.19 (d, J = 2.6, *p*), 129.66 (d, J = 10.9, *m*); 92.10 (s, C_5H_5), 34.06 (s, $\mathrm{ICH_2}C\mathrm{H_2}$), 31.90 (d, J = 3.1, ICH_2), 23.18 (s, $C\mathrm{H_2CH_3}$), 13.14 (s, CH_3)	11.3 (s)
 **3e**	ν_{NO} 1696	7.56–7.26 (m, 3 C_6H_5), 5.62 (s, C_5H_5), 2.80 (d, J = 11.9, $\mathrm{IC}H\mathrm{H'}$), 2.52 (d, J = 12.0, $\mathrm{ICH}H'$), 0.19 (s, $Si(CH_3)_3$)	PPh_3 at 133.56 (d, J = 11.0, *o*), 133.16 (d, J = 56.7, *i*), 132.12 (d, J = 2.7, *p*), 129.59 (d, J = 11.0, *m*); 92.40 (s, C_5H_5), 14.39 (d, J = 1.9, CH_2), −1.63 (s, 3 CH_3)	11.6 (s)
 **3f**	ν_{NO} 1691	7.55–7.26 (m, 3 C_6H_5), 5.65 (s, C_5H_5), 3.89 (d of t, J = 7.3, 7.1, $\mathrm{IC}H\mathrm{H'}$), 3.64 (m, 3 H, $\mathrm{ICH}H'$, CH_2Cl), 2.18 (pen, J = 6.9, 2 H, CCH_2C)	PPh_3 at 133.57 (d, J = 11.0, *o*), 133.14 (d, J = 57.0, *i*), 132.17 (d, J = 2.7, *p*), 129.63 (d, J = 11.0, *m*); 92.29 (s, C_5H_5), 43.88 (s, $\mathrm{CH_2}C\mathrm{H_2Cl}$), 34.35 (s, $\mathrm{ICH_2}C\mathrm{H_2}$), 25.99 (d, J = 3.0, ICH_2)	11.1 (s)
 **3g**	ν_{NO} 1718	7.56–7.25 (m, 3 C_6H_5), 5.70 (s, C_5H_5), 5.30 (d, J = 6.8, $\mathrm{IC}H\mathrm{H'}$), 5.06 (d, J = 6.8, $\mathrm{ICH}H'$)	PPh_3 at 133.45 (d, J = 11.0, *o*), 133.05 (d, J = 57.7, *i*), 132.18 (d, J = 2.4, *p*), 129.63 (d, J = 10.9, *m*); 92.54 (s, C_5H_5), 23.71 (d, J = 4.6, CH_2)	10.7 (s)
 **3h**	ν_{NO} 1688	7.69–7.29 (m, 4 C_6H_5), 5.48 (s, C_5H_5)	PPh_3 at 133.68 (d, J = 11.0, *o*), 133.18 (d, J = 57.2, *i*), 132.41 (d, J = 2.5, *p*), 129.86 (d, J = 11.0, *m*); C_6H_5I at 134.99 (s), 131.71 (s), 131.10 (s), 130.64 (s, *i*)	10.2 (s)
 **3i**	ν_{NO} 1695	7.58–7.30 (m, 3 C_6H_5 + $\mathrm{C_6}H_2\mathrm{H_2'}$), 6.86 (d, J = 9.1, $\mathrm{C_6H_2}H_2'$),[e] 5.46 (s, C_5H_5), 3.83 (s, CH_3)	PPh_3 at 133.66 (d, J = 11.5, *o*), 133.23 (d, J = 57.6, *i*), 132.33 (d, J = 2.8, *p*), 129.79 (d, J = 11.0, *m*); *p*-$CH_3OC_6H_4I$ at 162.07 (s, $C\mathrm{OCH_3}$), 136.28 (s), 117.48 (s), 116.69 (s, CI), 56.00 (s, OCH_3); 92.98 (s, C_5H_5)	10.2 (s)

Table I (Continued)

	IR,[a] cm^{-1}	^{1}H NMR,[b] δ	^{13}C{^{1}H} NMR,[c] ppm	^{31}P{^{1}H} NMR,[d] ppm
 **10**[f]		5.56 (s, C_5H_5), 4.18 (dq, J = 8.8, 7.3, BrC*H*H′), 3.73 (dq, J = 8.9, 7.4, BrCH*H*′), 1.62 (t, J = 7.2, CH_3)	91.86 (s, C_5H_5), 56.67 (s, CH_2), 17.84 (s, CH_3)	12.9 (s)
 **11**[g]		5.59 (s, C_5H_5), 4.43 (dq, J = 9.8, 7.1, ClC*H*H′), 3.92 (dq, J = 9.2, 7.4, ClCH*H*′), 1.54 (t, J = 7.3, CH_3)	91.47 (s, C_5H_5), 69.91 (d, J = 1.8, CH_2), 17.45 (s, CH_3)	13.6 (s)

[a] KBr pellet. [b] ^{1}H NMR spectra were taken at 300 MHz in CD_2Cl_2 at ambient probe temperature and were referenced to $CHDCl_2$ (5.32 ppm) unless noted. All couplings are to ^{1}H unless noted and are in hertz. [c] ^{13}C NMR spectra were taken at 75 MHz in CD_2Cl_2 at ambient probe temperature and were referenced to CD_2Cl_2 (53.8 ppm) unless noted. All couplings are to ^{31}P and are in hertz. Assignments of phenyl carbon resonances were made as described in footnote *c* of Table I in Buhro, W. E.; Georgiou, S.; Fernãndez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. [d] ^{31}P NMR spectra were taken externally locked at 32 MHz in CH_2Cl_2 at ambient probe temperature and were referenced to external H_3PO_4 unless noted. [e] Part of dd; other doublet obscured by C_6H_5 resonances. [f] All data for **10** are at −60 °C. [g] All data for **11** are at −40 °C.

resonance due to **3a** intensified and shifted somewhat as that of **2** diminished. At −50 °C, ≥90% conversion to **3a** occurred over the course of several hours. In experiments with less reactive alkyl iodides (see below), or at lower reactant concentrations, small amounts of a transient appeared (19.08 ppm, −40 °C; ^{1}H NMR, δ 5.48 vs TMS, −41 °C) and converted to product at higher temperatures.

Similar preparative reactions were conducted with α,ω-iodochloroalkanes $I(CH_2)_nCl$ (n = 3, **f**; 1, **g**). These gave alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I(CH_2)_nCl)]^+BF_4^-$ (**3f** and **3g**) in 63–64% yields after workup. Complexes **3f** and **3g** were characterized analogously to **3a–e** above. The ligation of rhenium to iodine as opposed to chlorine in 1,3-iodochloropropane complex **3f** was established by ^{13}C NMR. The free ligand exhibited resonances (ppm, CD_2Cl_2) at 3.16 (ICH_2), 35.85 (CCH_2C), and 45.38 (CH_2Cl).[18] The corresponding resonances in **3f** were found at 25.99 (d, J_{CP} = 3.0 Hz), 34.35, and 43.88 ppm (Table I). Only the iodide-substituted carbon exhibited a substantial downfield shift analogous to that observed for **3a–e** and was furthermore coupled to phosphorus. The structure of iodochloromethane complex **3g** was assigned by analogy to that of **3f**.

The preceding reactions with α,ω-iodochloroalkanes were monitored by ^{31}P NMR. Reaction of **2** and $I(CH_2)_3Cl$ occurred over the course of several hours at −40 °C. Complex **3f** (12.77 ppm) was by far the dominant product, with at best a trace resonance (13.40 ppm; ^{1}H NMR δ 5.66) that could possibly be assigned to a chlorine-ligated linkage isomer. The sample was warmed to 18 °C, and **3f** was present in 80–90% yield by ^{31}P NMR. The reaction of **2** and ICH_2Cl was similarly monitored. No resonance that could plausibly be attributed to a linkage isomer was observed, and **3g** formed in 70–80% NMR yields. Preparatively, somewhat better yields of **3g** were obtained when ICH_2Cl was added to methyl complex **1** *prior* to $HBF_4{\cdot}OEt_2$ addition.

Similar preparative reactions were conducted with aryl iodides $p\text{-}IC_6H_4X$ (X = **h**, H; **i**, OCH_3). These gave aryl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IAr)]^+BF_4^-$ (**3h** and **i**) in 66–72% yields after workup. Again, higher yields were obtained when the substrates were added to **1** prior to $HBF_4{\cdot}OEt_2$ addition. Complexes **3h** and **3i** were characterized analogously to **3a–g** above (Table I). The ReIC ^{13}C NMR resonances were again found to be deshielded relative to those of the free ligands, as shown in Chart II. No evidence for an aryl ether complex linkage isomer was noted during the formation of **3i**.

Table II. Rates of Reaction of Deuterodichloromethane Complex **2**-d_2 with Alkyl and Aryl Halides at −41.0 °C[a]

substrate	k_{obsd}, s^{-1} × 10^4	k_{rel}
ICH_3	3.07 ± 0.04	2.2
ICH_2CH_3	2.28 ± 0.03	1.7
$ICH_2CH_2CH_2Cl$	2.03 ± 0.04	1.5
ICH_2Cl	1.69 ± 0.22	1.2
$ICH(CH_3)_2$[b]	1.52 ± 0.05	1.1
$p\text{-}IC_6H_4OCH_3$	2.21 ± 0.10	1.6
IC_6H_5	1.37 ± 0.02	1.0
$BrCH_2CH_3$	0.72 ± 0.08	0.5

[a] All measurements were made under pseudo-first-order conditions in CD_2Cl_2 with $[\text{substrate}]_0$ = 0.25 M and $[\mathbf{2}]_0$ = ca. 0.02 M (see Experimental Section); a transient (δ 5.48) formed at ca. one-tenth the rate of the substrate complexes (see text). [b] Characterization of the isopropyl iodide complex will be reported in a separate paper.

Deuterodichloromethane complex **2–**d_2 was generated in CD_2Cl_2 analogously to **2**. Its rate of disappearance in the presence of excesses of several alkyl and aryl halides was monitored by ^{1}H NMR. Data are summarized in Table II. Interestingly, the most reactive iodide substrate (methyl iodide) differs from the least reactive (phenyl iodide) by only a factor of 2.2. In separate studies,[8b,19] we have found k_{obsd} for substitution reactions of **2**-d_2 to depend upon ligand concentrations, with no evidence for "saturation kinetics" regimes.

2. Crystal Structures of Alkyl Iodide Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-{\cdot}(CH_2Cl_2)_{0.5}$ [3e·$(CH_2Cl_2)_{0.5}$] and Iodide Complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(I)$ (4). We sought to verify the structures of alkyl iodide complexes **3** by X-ray crystallography. However, repeated difficulty was encountered in growing suitable crystals, or in solving data sets due to disorder problems. Finally, X-ray data were collected on crystals of (trimethylsilyl)methylene iodide complex **3e**·$(CH_2Cl_2)_{0.5}$ as summarized in Table III. Refinement, described in the Experimental Section, yielded the structure shown in Figure 1, the bond lengths and angles listed in Tables IV and V, and the atomic coordinates given in the supplementary material. Thermal parameters and structure factors were included in our earlier communication.[7a] The P-Re-I-C1 and N-Re-I-C1 torsion angles were found to be 168.9 (5) and 77.5 (9)°, respectively, indicating an approxi-

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(18) Assignments made from: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, fourth ed.; Wiley: New York; 1981; p 261, Table III; p 269, Table XI.

(19) Garner, C. M., University of Utah, unpublished results.

Table III. Summary of Crystallographic Data for Alkyl Iodide Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-\cdot(CH_2Cl_2)_{0.5}$ [**3e**$\cdot(CH_2Cl_2)_{0.5}$] and Iodide Complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(I)$ (**4**)

	3e$\cdot(CH_2Cl_2)_{0.5}$	**4**
molecular formula	$C_{27}H_{31}BF_4INOPReSi\cdot(CH_2Cl_2)_{0.5}$	$C_{24}H_{22}INOPRe$
MW	886.98	684.53
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
cell dimens (15 °C)		
a, Å	9.747 (2)	9.152 (1)
b, Å	12.779 (3)	14.046 (3)
c, Å	13.938 (3)	18.063 (3)
α, deg	88.73 (2)	
β, deg	92.22 (2)	
γ, deg	111.23 (2)	
V, Å³	1617.0	2322.0
Z	2	4
d_{obsd}, gm/cm³ (22 °C)	1.808	1.942
d_{calcd}, gm/cm³ (15 °C)	1.82	1.958
crystal dimens, mm	0.36 × 0.23 × 0.18	0.25 × 0.21 × 0.10
diffractometer	Syntex $P\bar{1}$	Syntex $P\bar{1}$
radiation, Å	Mo Kα (0.71073)	Mo Kα (0.71073)
collectn temp, °C	15 (1)	15 (1)
data collectn method	θ–2θ	θ–2θ
scan speed, deg/min	variable, 3.0–12.0	variable, 3.0–8.0
reflctns measd	5140	2645
range/indices	*h*(0,10), *k*(−14,14), *l*(−15,15)	*h*(0,11), *k*(0,17), *l*(0,22)
scan range	$K_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0	$k_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0
2θ limit, deg	3.0–47.0	2.0–52.0
total bkdg. time/scan time	0.5	0.5
no. of reflctns between std	97	98
total no. of unique data	4388	2645
obsd data, $I > 3\sigma(I)$	3669	2225
abs coeff, cm⁻¹	49.78	67.02
min absorptn correctn	55.89	44.11
max absorptn correctn	99.92	99.19
no. of variables	343	262
R (averaging)	0.022, 0.014	
Δ/σ (max)	0.0	0.002
$R = \sum(\lvert F_o - F_c\rvert)/\sum(F_o)$	0.0438	0.0411
$R_w = \sum(\lvert F_o - F_c\rvert)w^{1/2}/\sum\lvert F_o\rvert w^{1/2}$	0.0541	0.0452
goodness of fit	3.12	2.60
$\Delta\rho$ (max), eÅ⁻³	1.17, 0.924 Å from Re	1.29, 1.22 Å from Re

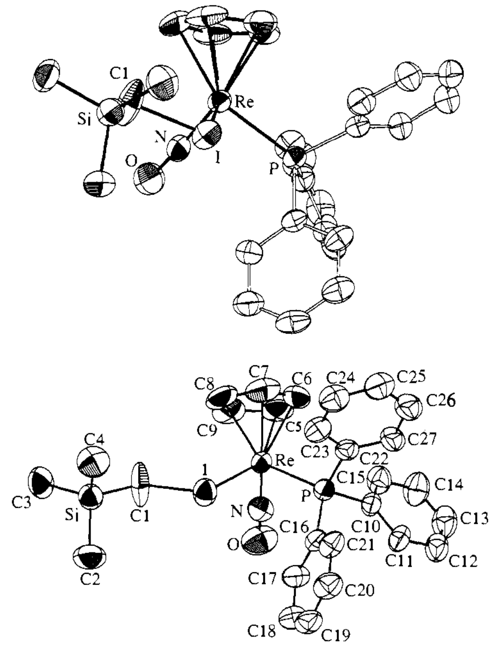


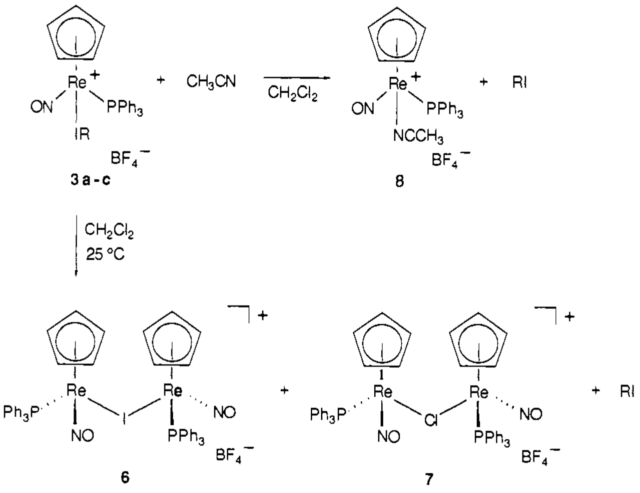
Figure 1. Two views of the cation of alkyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-\cdot(CH_2Cl_2)_{0.5}$ [**3e**$\cdot(CH_2Cl_2)_{0.5}$].

mately anti relationship of the Ph_3P and $CH_2Si(CH_3)_3$ substituents about the Re–I bond. The Re–I–C1–Si torsion angle was 173.8 (7)°, indicating an anti relationship of the bulky silicon and rhenium substituents about the I–C1 bond.

Table IV. Bond Lengths in **3e**$\cdot(CH_2Cl_2)_{0.5}$ and **4** (Å)

atom 1	atom 2	**3e**$\cdot(CH_2Cl_2)_{0.5}$	**4**
Re	I	2.678 (1)	2.7210 (9)
Re	P	2.385 (3)	2.355 (3)
Re	N	1.740 (9)	1.770 (9)
I	C1	2.18 (1)	
Si	C1	1.88 (2)	
Si	C2	1.86 (2)	
Si	C3	1.87 (2)	
Si	C4	1.87 (2)	
N	O	1.20 (1)	1.18 (1)
Re	C5	2.27 (2)	2.26 (1)
Re	C6	2.26 (2)	2.31 (1)
Re	C7	2.27 (1)	2.32 (1)
Re	C8	2.30 (1)	2.27 (1)
Re	C9	2.30 (2)	2.22 (1)
C5	C6	1.42 (2)	1.40 (2)
C5	C9	1.47 (2)	1.45 (2)
C6	C7	1.41 (3)	1.40 (2)
C7	C8	1.40 (3)	1.37 (2)
C8	C9	1.42 (3)	1.40 (2)
C5	C28		1.54 (2)
P	C10	1.84 (1)	1.82 (1)
P	C16	1.83 (1)	1.822 (9)
P	C22	1.83 (1)	1.83 (1)
C10	C11	1.40 (2)	1.40 (1)
C10	C15	1.39 (2)	1.38 (1)
C11	C12	1.42 (2)	1.37 (2)
C12	C13	1.39 (3)	1.37 (2)
C13	C14	1.36 (2)	1.34 (2)
C14	C15	1.40 (2)	1.39 (1)
C16	C17	1.40 (2)	1.42 (1)
C16	C21	1.40 (2)	1.41 (1)
C17	C18	1.41 (2)	1.38 (1)
C18	C19	1.39 (2)	1.39 (2)
C19	C20	1.39 (2)	1.39 (2)
C20	C21	1.41 (2)	1.39 (2)
C22	C23	1.40 (2)	1.39 (1)
C22	C27	1.40 (2)	1.38 (1)
C23	C24	1.40 (2)	1.39 (1)
C24	C25	1.40 (2)	1.34 (2)
C25	C26	1.40 (2)	1.39 (2)
C26	C27	1.41 (2)	1.41 (2)

Scheme II. Thermal and Solvent Stability of Alkyl Iodide Complexes



In order to better analyze the bonding in **3e**$\cdot(CH_2Cl_2)_{0.5}$, structural data on related compounds were sought. We were not able to obtain suitable crystals of iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**5**),[20] or its optically active analogue. However,

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[20] Merrifield, J. H.; Fernāndez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

Table V. Bond Angles in **3e**·$(CH_2Cl_2)_{0.5}$ and **4** (degrees)

atom 1	atom 2	atom 3	**3e**·$(CH_2Cl_2)_{0.5}$	**4**
I	Re	P	91.82 (9)	92.96 (6)
I	Re	N	97.0 (4)	99.0 (3)
P	Re	N	91.1 (3)	94.6 (2)
Re	I	C1	102.5 (5)	
Re	N	O	177 (1)	174.1 (9)
I	Re	C5	147.8 (4)	136.5 (3)
I	Re	C6	133.7 (4)	100.8 (4)
I	Re	C7	98.3 (5)	85.5 (4)
I	Re	C8	88.0 (5)	105.2 (4)
I	Re	C9	111.9 (5)	141.4 (4)
P	Re	C5	115.1 (4)	126.8 (3)
P	Re	C6	90.5 (4)	152.6 (3)
P	Re	C7	100.5 (4)	124.4 (4)
P	Re	C8	135.3 (5)	94.6 (3)
P	Re	C9	150.9 (5)	93.6 (4)
N	Re	C5	99.7 (5)	94.9 (4)
N	Re	C6	129.2 (6)	106.4 (4)
N	Re	C7	160.5 (6)	140.6 (4)
N	Re	C8	133.3 (6)	153.6 (4)
N	Re	C9	101.9 (5)	118.4 (5)
I	C1	Si	114.5 (9)	
C1	Si	C2	109.6 (9)	
C1	Si	C3	104.0 (8)	
C1	Si	C4	109.6 (8)	
C2	Si	C3	109.6 (8)	
C2	Si	C4	111.9 (9)	
C3	Si	C4	111.8 (7)	
C5	C6	C7	109 (1)	107 (1)
C5	C9	C8	106 (1)	106 (1)
C6	C5	C9	107 (1)	108 (1)
C6	C7	C8	108 (2)	109 (1)
C7	C8	C9	110 (2)	110 (1)
C6	C5	C28		129 (1)
C9	C5	C28		123 (1)
Re	P	C10	113.3 (4)	110.3 (3)
Re	P	C16	117.0 (4)	115.2 (3)
Re	P	C22	113.6 (4)	121.1 (3)
P	C10	C11	120 (1)	121.5 (8)
P	C10	C15	119.5 (8)	119.8 (9)
P	C16	C17	118 (1)	121.1 (8)
P	C16	C21	121.6 (9)	120.2 (8)
P	C22	C23	118 (1)	119.0 (8)
P	C22	C27	120.7 (9)	122.9 (8)
C10	P	C16	101.9 (5)	105.9 (5)
C10	P	C22	105.0 (6)	103.5 (4)
C16	P	C22	104.6 (6)	99.1 (5)
C10	C11	C12	119 (1)	121 (1)
C10	C15	C14	120 (1)	119 (1)
C11	C12	C13	119 (1)	118 (1)
C11	C10	C15	120 (1)	119 (1)
C12	C13	C14	121 (1)	122 (1)
C13	C14	C15	120 (2)	121 (1)
C16	C17	C18	121 (1)	121 (1)
C16	C21	C20	119 (1)	119 (1)
C17	C18	C19	119 (1)	120 (1)
C17	C16	C21	120 (1)	118.4 (9)
C18	C19	C20	121 (1)	119 (1)
C19	C20	C21	121 (1)	122 (1)
C22	C27	C26	118 (1)	121 (1)
C22	C23	C24	120 (1)	122 (1)
C23	C24	C25	120 (1)	119 (1)
C23	C22	C27	121 (1)	118 (1)
C24	C25	C26	120 (1)	122 (1)
C25	C26	C27	121 (1)	118 (1)
F1	B	F2	101 (2)	
F1	B	F3	109 (2)	
F1	B	F4	107 (2)	
F2	B	F3	109 (2)	
F2	B	F4	109 (2)	
F3	B	F4	120 (2)	

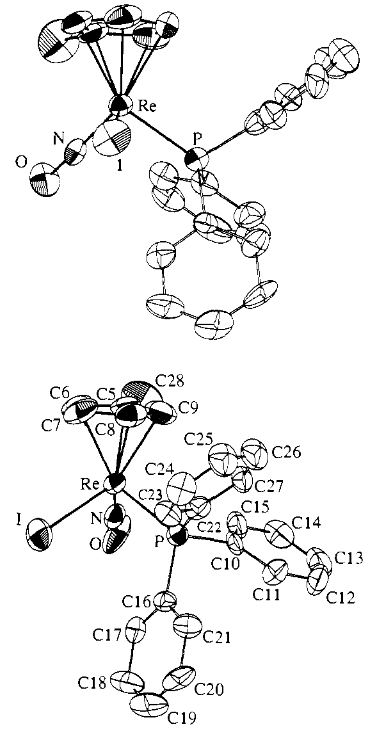

Figure 2. Two views of the molecular structure of iodide complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(I) (**4**).

good crystals of *methyl*cyclopentadienyl iodide complex (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(I) (**4**)[14] were obtained, and X-ray data were collected as outlined in Table III. Refinement gave the structure shown in Figure 2, the bond lengths and angles listed in Tables IV and V, and the atomic coordinates given in the supplementary material. The crystal structure of *bridging* iodide complex (*RR*,*SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)]$_2$I$^+BF_4^-$ (**6**; see Scheme II) has been reported separately[7b] and is contrasted with those of **3e**·$(CH_2Cl_2)_{0.5}$ and **4** below.

3. Thermal and Solvent Stability of Alkyl and Aryl Iodide Complexes. Alkyl iodide complexes **3a–c** decomposed over 48–60 h in CD_2Cl_2 at 25 °C to mixtures (Scheme II) of bridging iodide complex (*RR*,*SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)]$_2$I$^+BF_4^-$ (**6**, 43–65%), bridging chloride complex (*SS*,*RR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)]$_2$Cl$^+BF_4^-$ (**7**, 29–48%), alkyl iodides (25–60%), and an unidentified minor product [6–10%; ^{1}H NMR, δ 6.03 (C_5H_5)]. Product identities were assigned by ^{1}H and ^{31}P NMR, and yields were determined by integration vs an internal standard. The independent preparation and characterization of **6** and **7** has been described elsewhere.[7b,8] Phenyl iodide complex **3h** decomposed under analogous conditions to a multitude of products (^{31}P NMR), of which **7** was a major component and **6** was at most a very minor component.

Alkyl and aryl iodide complexes **3** were insoluble in hydrocarbon and ethereal solvents. In the presence of solvents more polar than CH_2Cl_2, displacement reactions generally occurred. For example, complexes **3a–c** reacted with CH_3CN (2 equiv, 0.05–0.09 M in CD_2Cl_2) over 19–24 h to give acetonitrile complex [(η^5-C_5H_5)Re(NO)(PPh_3)($NCCH_3$)]$^+BF_4^-$ (**8**, 82–87%)[21] and free alkyl iodides (72–82%). Small amounts of bridging halide complexes **6** and **7** also formed from the independent decomposition of **3a–c** on this time scale (Scheme II). Product identities and yields were determined as above, and the formation of alkyl iodides was confirmed by GLC. Phenyl iodide complex **3h** reacted similarly with CH_3CN (3 equiv, 0.09 M in CD_2Cl_2), and at only a slightly faster rate than **3a**.

Methyl iodide complex **3a** (0.020 M in CD_2Cl_2) was treated with 15 equiv of CD_3I at 298 °C. Deuteromethyl iodide complex [(η^5-C_5H_5)Re(NO)(PPh_3)(ICD_3)]$^+BF_4^-$ (**3a**-d_3) formed with k_{obsd} = (2.26 ± 0.13) × 10^{-5} s^{-1}.[22] This corresponds to a half-life of

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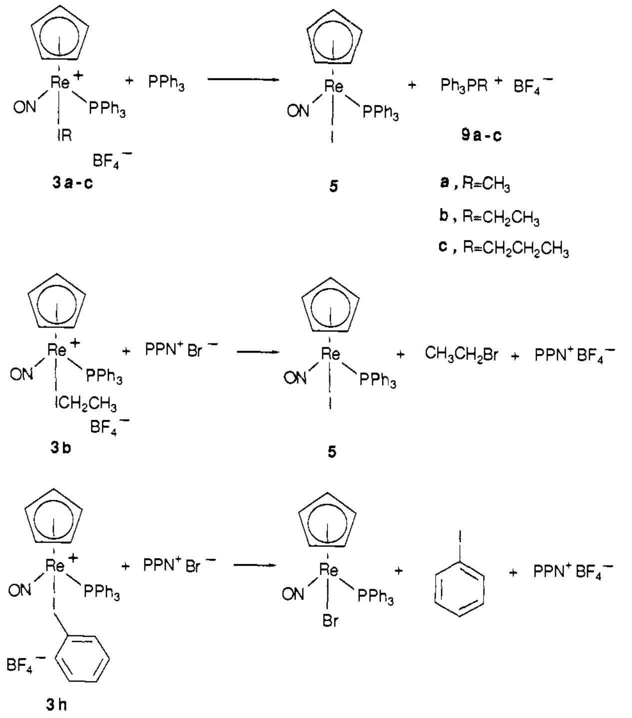
[21] Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

[22] (a) The first-order k_{obsd} is consistent with either a dissociative or associative exchange mechanism.[22b] Experiments to distinguish these possibilities are in progress. (b) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw Hill: New York, 1981; pp 16–21, 50–55.

Scheme III. Reactions of Nucleophiles with Alkyl and Aryl Iodide Complexes



8.5 h. Hence, alkyl iodide ligands do not undergo particularly rapid exchange at room temperature.

4. Reactions of Alkyl and Aryl Iodide Complexes with Nucleophiles. We sought to probe the reactivities of the alkyl and aryl iodide ligands toward nucleophiles, Alkyl iodide complexes **3a–c** (0.36–0.44 M in $CDCl_3$) were treated with PPh_3 (1.2 equiv; 0,43–0,53 M) at 25 °C. In each case, reaction was complete within 15 min, as assayed by ^1H and ^{31}P NMR (Scheme III). Substitution occurred at the alkyl iodide carbon to give iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**5**)[20] and phosphonium salts $Ph_3PR^+BF_4^-$ (**9a–c**) in >99–92% and 86–93% yields, respectively (determined by ^1H NMR integration vs an internal standard). The identities of the phosponium salts, two of which had been reported previously,[23] were verified by comparisons with independently prepared samples (Experimental Section).

A qualitative comparison of the reactivity of *free* alkyl iodides was sought. Hence, methyl iodide, ethyl iodide, and *n*-propyl iodide (0.52–0.53 M in $CDCl_3$) were treated with PPh_3 (0.75–0.90 equiv; 0.39–0.47 M) under analogous conditions. Conversions to phosphonium salts $Ph_3PR^+I^-$ were 70 ± 2% complete after 4 h, 9 ± 2% complete after 18 h, and ≤2% complete after 18 h, respectively. Hence, alkyl iodides are dramatically activated toward nucleophilic attack upon coordination to the Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I).

The rate of reaction of ethyl iodide complex **3b** and PPh_3 in $CDCl_3$ was monitored by ^1H NMR at temperatures between −55 and −30 °C. The reaction exhibited second-order kinetics, and rate constants were obtained by standard methods.[22b] Data are summarized in Table VI. These give $\Delta H^\ddagger = 12.9 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -12.0 \pm 0.9$ eu, and an extrapolated rate at 298 K of 5.3 ± 1.7 $M^{-1}\ s^{-1}$.

The rate of the much slower reaction of *free* ethyl iodide and PPh_3 in $CDCl_3$ was monitored at temperatures between 45 and 60 °C. This reaction also exhibited the expected second-order kinetics, and data are summarized in Table VI. These give $\Delta H^\ddagger = 16.3 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -25.9 \pm 1.5$ eu, and an extrapolated rate at 298 K of $(1.6 \pm 0.1) \times 10^{-5}\ M^{-1}\ s^{-1}$. *Hence, coordination of ethyl iodide to Lewis acid I results in a* $(3.3 \pm 1.3) \times 10^5$ *rate acceleration for nucleophilic attack by* PPh_3 *at 298 K!*

Table VI. Rates of Reaction of PPh_3 with Free and Coordinated Ethyl Iodide in $CDCl_3$

temp, K	[**3b**] or $[C_2H_5I]$, M	$[PPh_3]$, M	*k*, $M^{-1}\ s^{-1}$
(A) Reaction of PPh_3 and Ethyl Iodide Complex **3b**			
218	0.0547	0.111	$(1.32 \pm 0.02) \times 10^{-3}$
223	0.0549	0.111	$(2.44 \pm 0.04) \times 10^{-3}$
228	0.0554	0.114	$(6.02 \pm 0.31) \times 10^{-3}$
233	0.0550	0.112	$(8.34 \pm 0.33) \times 10^{-3}$
238	0.0530	0.112	$(1.92 \pm 0.03) \times 10^{-2}$
243	0.0528	0.111	$(3.02 \pm 0.03) \times 10^{-2}$
228	0.0527	0.0550	$(6.29 \pm 0.03) \times 10^{-3}$
228	0.0277	0.111	$(6.03 \pm 0.24) \times 10^{-3}$
228	0.0290	0.111	$(5.66 \pm 0.33) \times 10^{-3}$
(B) Reaction of PPh_3 and Ethyl Iodide			
318	0.0544	0.109	$(0.94 \pm 0.03) \times 10^{-4}$
323	0.0544	0.109	$(1.48 \pm 0.03) \times 10^{-4}$
328	0.0550	0.111	$(2.17 \pm 0.05) \times 10^{-4}$
333	0.0544	0.109	$(3.16 \pm 0.10) \times 10^{-4}$
333	0.0556	0.223	$(2.86 \pm 0.03) \times 10^{-4}$
333	0.111	0.111	$(3.30 \pm 0.04) \times 10^{-4}$

No ^{31}P NMR evidence for the formation of iodide complex **5** or phosphonium salts ($Ph_4P^+BF_4^-$, $Ph_3PCH_2Cl^+BF_4^-$) was noted when phenyl iodide complex **3h** was treated with PPh_3 in CH_2Cl_2. A number of products formed over the course of 24 h at 25 °C.

Alkyl bromides and chlorides generally react with NaI in acetone to give alkyl iodides (Finkelstein reaction).[24] Although procedures have been developed for the conversion of alkyl iodides to alkyl bromides and chlorides,[25] we sought to determine whether such "reverse Finkelstein" reactions might be accomplished via alkyl iodide complexes. Hence, ethyl iodide complex **3b** was treated with PPN^+Br^- (1.2 equiv; $PPN^+ = Ph_3P{=}N{=}PPh_3^+$) in CD_2Cl_2 at room temperature in the presence of Ph_3SiCH_3 standard (Scheme III). An immediate color change occurred, and a ^1H NMR spectrum showed the reaction to be complete within 5 min. Ethyl bromide and iodide complex **5** formed in 84% and 96% yields, respectively (average of two runs). Their identities were confirmed by ^{13}C NMR and ^{31}P NMR. The only other product detectable by NMR was $PPN^+BF_4^-$ (^{31}P NMR, 21.5 ppm).

Phenyl iodide complex **3h** was similarly treated with PPN^+Br^-. An immediate color change again occurred, and a ^{31}P NMR spectrum showed the reaction to be complete within 5 min. Bromide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$ (^{31}P NMR, 16.1 ppm)[20] and $PPN^+\ BF_4^-$ were the only phosphorus-containing products. Phenyl iodide formed in 85% yield, as assayed by GLC vs an internal standard and qualitatively confirmed by ^{13}C NMR. Hence, coordinated aryl iodides do not undergo nucleophilic substitution.

5. Generation of Ethyl Bromide and Ethyl Chloride Complexes. The preparation of alkyl bromide and chloride complexes was briefly examined. First, deuterodichloromethane complex **2**-d_2 was generated in a NMR tube and treated with ethyl bromide (3.0 equiv) under conditions analogous to those in Scheme I. Ethyl bromide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(BrCH_2CH_3)]^+BF_4^-$ (**10**) formed in high spectroscopic yield at −40 to −30 °C and subsequently decomposed over the course of several hours at 0 °C. Rate experiments (Table II) showed ethyl bromide to be 3,4 times *less* reactive than ethyl iodide at −41 °C. NMR data are summarized in Table I.

Complex **2**-d_2 was similarly treated with ethyl chloride (7.0 equiv). The sample was kept at −40 °C for several hours, after which time **2**-d_2 and ethyl chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2CH_3)]^+BF_4^-$ (**11**) were present in a (60 ±

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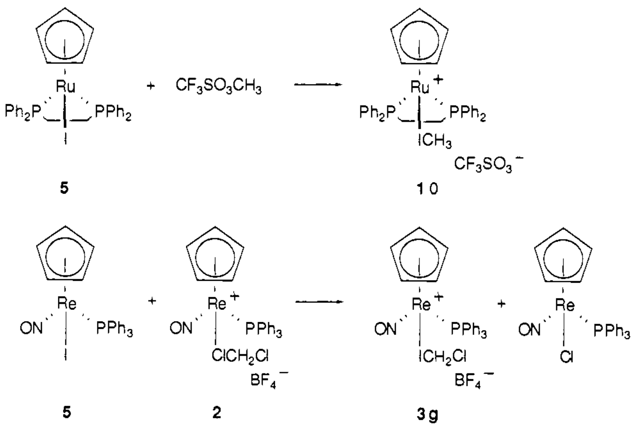
[23] (a) Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1610. (b) Horner, L.; Nippe, B. *Chem. Ber.* **1958**, *91*, 67.

[24] (a) Hudlicky, M.; Hudlicky, T. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Supplement D, Part 2, pp 1021–1172. (b) Smith, W. B.; Branum, G. D. *Tetrahedron Lett.* **1981**, *22*, 2055.

[25] (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 307–308, 381–382. (b) Willy, E. W.; McKean, D. R.; Garcia, B. A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1989. (c) Hahn, R. C. *J. Org. Chem.* **1988**, *53*, 1331.

Scheme IV. Alkylation of Metal Iodide Complexes



5):(40 ± 5) ratio. The amount of **11** present did not increase with additional time or warming, and **11** decomposed over the course of 1 h at 0 °C. NMR data are summarized in Table I.

Ethyl halide complexes **3b**, **10**, and **11** exhibit several conspicuous spectroscopic trends (Table I). For example, the PPh_3 ^{31}P NMR resonances and the XCH_2 ^{13}C and ^1H NMR resonances shift progressively downfield, whereas the CH_3 ^1H and ^{13}C NMR resonances shift upfield. The XCH_2 ^{13}C NMR resonances of **10** and **11** are 28 and 30 ppm downfield, respectively, of those of the free ethyl halides (28.3 and 39.9 ppm, neat).[18]

Discussion

1. Synthesis of Alkyl and Aryl Halide Complexes. The above data establish the ready availability of a variety of primary alkyl iodide and aryl iodide complexes. Studies in progress show that secondary alkyl iodide complexes can be generated in high spectroscopic yield. However, as anticipated from steric factors, they form more slowly [e.g., $ICH_3 > ICH_2CH_3 > ICH(CH_3)_2$; Table II], and are less readily isolated. No adduct is observed by NMR upon addition of *tert*-butyl iodide to dichloromethane complex **2**.

The data on the reactions of **2** with ethyl halides and α,ω-iodochloroalkanes establish the reactivity order RI > RBr > RCl. Although we are unaware of any study of the relative nucleophilicities of alkyl halides, this trend is expected based upon the order of gas-phase basicities.[3] Our present data do not rigorously establish a thermodynamic trend for alkyl halide binding to Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I). However, the binding constants of alkyl iodides and bromides are clearly much greater than those of CH_3CH_2Cl and CH_2Cl_2 and likely follow the order of gas-phase basicities.

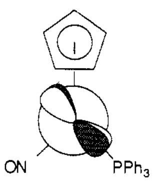
We have separately reported an analogous synthesis of *pentamethyl*cyclopentadienyl methyl iodide complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ICH_3)]^+BF_4^-$.[9] This species forms much more rapidly from its dichloromethane complex precursor than analogue **3a**. It is also less stable in solution and has not yet been isolated in analytically pure form. These trends may result from the diminished Lewis acidity of the $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$ fragment, as the pentamethylcyclopentadienyl ligand is considerably more electron releasing than the cyclopentadienyl ligand.[26] Studies in progress also show that *carbonyl*-substituted alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(IR)]^+X^-$ are easily generated.

Kulawiec and Crabtree recently reported the synthesis of ruthenium methyl iodide complex $[(\eta^5\text{-}C_5H_5)Ru(dppe)(ICH_3)]^+CF_3SO_3^-$ by alkylation of the corresponding iodide complex with $CF_3SO_3CH_3$ (Scheme IV).[10] This carbon–iodine bond-forming reaction constitutes a fundamentally different route to alkyl halide complexes and provides a second well-characterized class of 1:1 adducts. We have made the related observation that dichloromethane complex **2** alkylates iodide complex **5** to give iodochloromethane complex **3g**, as shown in Scheme IV.[7b] The 2:1 adduct $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$ (Chart I) is prepared in high yield by the hydrogenation of $[(COD)Ir(PPh_3)_2]^+X^-$ in 8:1 (v/v) CH_2Cl_2/CH_3I.[5]

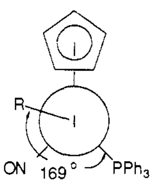
Finally, the question remains as to why alkyl halides, which are feeble bases toward H^+ and Li^+,[3] so readily form adducts with the rhenium Lewis acid I. Further, dichloromethane complex **2** can be generated in the presence of 25 equiv of ether,[8b] which is a much stronger base.[3] Also, the iodine atom in $p\text{-}IC_6H_4OCH_3$ reacts more rapidly with **2** than the ether oxygen. Hence, alkyl halide complexes of I appear to have either special kinetic accesibility or unusually high binding constants. Experiments designed to probe these possibilities are in progress.

2. Structural Aspects of Alkyl Iodide Complexes. (Trimethylsilyl)methylene iodide complex $\mathbf{3e}\cdot(CH_2Cl_2)_{0.5}$, bridging iodide complex $(RR,SS)\text{-}[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**6**; Scheme II), and iodide complex $(\eta^5\text{-}C_5H_4CH_3)Re(NO)(PPh_3)(I)$ (**4**) provide a series of closely related, crystallographically characterized compounds. The rhenium atoms bear *formal* positive, half-positive, and neutral charges, respectively. The iodine atoms bear two, two, and three lone electron pairs, respectively. Table IV shows that the rhenium–iodine bond lengthens upon going from $\mathbf{3e}\cdot(CH_2Cl_2)_{0.5}$ [2.678 (1) Å] to **4** [2.7210 (9) Å].[27] The rhenium–iodine bond lengths in **6** are intermediate [2.700 (2), 2.692 (2) Å].[7b] This trend is opposite to that expected from simple electrostatic considerations, as the Lewis acid fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$(I) should have a greater attraction to the anionic base I^- than the neutral base RI.[28]

Repulsive interactions between filled metal d orbitals and ligand lone electron pairs have been previously invoked to rationalize metal–ligand bond length trends.[28,29] Lewis acid I has been shown to have the high-lying d orbital HOMO depicted in II.[15,30] Also, Lewis base adducts of I lack low-lying acceptor orbitals on rhenium.[15,29] Since **4** has the greatest number of electron pairs on iodine, and no rhenium–iodine conformations that can diminish overlap with the occupied rhenium d orbital shown in II, rhenium–iodine repulsive interactions should be maximized. We presently believe that this best accounts for the longer rhenium–iodine bond in **4**.



II



III

The carbon–iodine bond in $\mathbf{3e}\cdot(CH_2Cl_2)_{0.5}$ [2.18 (1) Å] is at best very slightly longer than that in ethyl iodide [2.139 (5) Å].[31] A computer search of the Cambridge crystallographic files located 51 structurally characterized compounds with a $C\text{–}CH_2I$ unit, including one somewhat related to the alkyl iodide ligand in **3e**, Ph_3SnCH_2I [C–I 2.134 (7) Å].[32] The mean carbon–iodine bond length was 2.13 Å, with a standard deviation of 0.07 Å.

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(26) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(27) A computer search of the Cambridge crystallographic files located nine structurally characterized rhenium complexes with a terminal iodide ligand and an oxidation state range of Re(I) through Re(III). The mean rhenium–iodine bond length was 2.80 Å, with a standard deviation of 0.05 Å.

(28) Similar bond length trends are found in related phosphorus-containing complexes, which have been more extensively studied. For example, the $Re\text{–}PPh_2$ bond length in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2)$ is 2.461 (3) Å,[28] whereas the $Re\text{–}PH_2(t\text{-}C_4H_9)$ bond length in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PH_2(t\text{-}C_4H_9))]^+Cl^-$ is 2.361 (2) Å (Zwick, B. D.; Dewey, M. A.; Arif, A. M., University of Utah, unpublished results). The $Re\text{–}PPh_3$ bond lengths in these compounds are 2.358 (3) and 2.370 (2) Å, respectively.

(29) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(30) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (c) Schilling, B. E. R.; Hoffmann, R.; Faller, J. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(31) Kasuya, T.; Oka, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 296.

(32) Harrison, P. G.; Molloy, K. *J. Organomet. Chem.* **1978**, *152*, 53.

The geometry about iodine in **3e**·$(CH_2Cl_2)_{0.5}$ is also of interest. Bond angles in iodonium salts $RR'I^+X^-$ are typically ca. 95°, and short I^+/X^- "secondary bonds" are usually found.[33] In contrast, the Re–I–Cl bond angle in **3e**·$(CH_2Cl_2)_{0.5}$ is 102.5 (5)°, and all BF_4^- fluorine atoms are greater than 4.00 Å from iodine. The Re–I–Re bond angle in **6**, in which there is considerable steric interaction between ligands on the two rheniums, is 114.14 (4)°. A theoretical study of the coordinatively unsaturated platinum methyl iodide complex *trans*-$[(H_3N)_2Pt(C_6H_5)(ICH_3)]^+$ predicted a Pt–I–C bond angle of 100°.[34]

Finally, the conformation about the rhenium–iodine bond in **3e**·$(CH_2Cl_2)_{0.5}$ places the $(CH_3)_3SiCH_2$ substituent in the sterically less congested region between the small nitrosyl and medium-sized cyclopentadienyl ligands,[29b,35] as shown in III. Interestingly, this conformation also allows the possibility of back-bonding from the d orbital HOMO shown in II to the vacant carbon–iodine σ^* orbital. Such d → σ^* back-bonding has been previously proposed to occur in alkyl halide[5b] and related[36] complexes. Structural consequences would include a lengthened carbon–iodine bond and a shortened rhenium–iodine bond. In view of the small experimental bond length pertubations noted above, this issue has been probed in detail from a theoretical standpoint, as will be described in a subsequent paper.[15]

3. Reactivity of Alkyl and Aryl Iodide Complexes. The data in Table VI show that alkyl iodides are dramatically activated toward nucleophilic attack upon coordination to rhenium Lewis acid I. Crabtree has also found $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$ and $[(\eta^5\text{-}C_5H_5)Ru(dppe)(ICH_3)]^+CF_3SO_3^-$ to be reactive methylating agents.[5b,10] The former is at least 50 (and probably more than 10^4) times more reactive than methyl iodide toward $N(C_2H_5)_3$.[5b] Dichloromethane complexes $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ are readily attacked by halide nucleophiles X^- at −40 °C to give dihalomethanes XCH_2Cl and chloride complexes $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(Cl)$.[8b,9] Hence, alkyl halide complexes promise new avenues of flexibility in organic functional group manipulations, such as illustrated by the "reverse Finkelstein" reaction in Scheme III.

The polarity of a carbon–halide bond should increase upon coordination of the halide to a Lewis acid. Hence, the enhanced S_N2 reactivity of **3a–c** might simply be attributed to increased carbon electrophilicity and halide leaving group ability. However, theoretical studies to be reported in a subsequent paper suggest a novel, nonclassical substitution reaction coordinate.[15]

Nucleophiles that are not readily alkylated, such as CH_3CN, displace the alkyl halide ligands from **3a–i**. However, some anionic nucleophiles also effect displacement. For example, cyanide ion reacts with dichloromethane complex **2** to give chiefly cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$.[8b] Crabtree finds that the methyl iodide ligand in $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+$ is generally displaced by anionic nucleophiles, whereas that in $[(\eta^5\text{-}C_5H_5)Ru(dppe)(ICH_3)]^+$ is generally attacked at carbon.[5,10] These chemoselectivity trends are not at present understood.

The thermal behavior of **3a–i** is of fundamental interest. Interestingly, alkyl iodide oxidative addition *appears* not to be a significant decomposition pathway, although such reactivity is exhibited by the more electron rich and easily oxidized *pentamethyl*cyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ in CH_2Cl_2 at −35 °C.[9] The decomposition conditions in Scheme II are not ideal for mechanistic study, as bridging chloride complex **7** may form via equilibration of **3a–i** with dichloromethane complex **2**.[8] Indeed, there are only a few common solvents that dissolve **3a–i** but remain inert over reasonable periods of time; of these, the best candidate for mechanistic work is probably chlorobenzene. We hope that with the proper choice of conditions, it will be possible to quantify the effect of metal coordination upon carbon–halogen bond homolysis and heterolysis rates.

4. Conclusion. This study has demonstrated that alkyl iodide complexes are easily prepared in high yields and display extraordinary reactivity toward nucleophiles. The coordination of alkyl halides to metals provides a new generation of leaving groups that can be sterically and electronically tailored and rendered chiral. Since dichloromethane complex **2** is easily generated in optically pure form and reacts with a variety of Lewis bases with retention of configuration,[8] complexes **3a–i** should be readily available in optically pure form. Additional reactions of these compounds, including studies of their utility in asymmetric organic synthesis, will be described in future publications.

Experimental Section

General Data. All reactions were carried out under a dry nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. NMR spectra were recorded on Varian XL-300 (^1H, ^{13}C, ^{31}P) and FT-80A (^{31}P) spectrometers as outlined in Table I. Mass spectra were obtained on a VG 770 spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories. Melting points were determined in evacuated capillaries and were not corrected.

Solvents were purified as follows: CH_2Cl_2 and $CHCl_3$, distilled from P_2O_5; benzene, ether, and tetrahydrofuran, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$ and CD_2Cl_2, vacuum transferred from CaH_2. The following reagents were used as received unless noted: HBF_4·Et_2O (Aldrich; standardized at ca. −80 °C in CD_2Cl_2 as previously described),[8b] PPh_3 (Pressure), $Ph_3PR^+I^-$ (Aldrich), PPN^+Br^- and PPN^+I^- (Strem), Ph_3SiCH_3 (Pfaltz and Bauer), and alkyl and aryl halides (Aldrich or Fluka).

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPb_3)(ICH_3)]^+BF_4^-$ (3a). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**; 0.187 g, 0.335 mmol),[16] CH_2Cl_2 (20 mL), and a stir bar and was fitted with a septum. The solution was cooled to −78 °C and stirred. Then HBF_4·Et_2O (0.045 mL, 0.35 mmol) and CH_3I (0.085 mL, 1.365 mmol) were sequentially added via syringe. The solution was allowed to warm to room temperature and was kept at room temperature for 0.5 h. Hexane (50 mL) was added, and a tan powder precipitated. The powder was precipitated twice more from CH_2Cl_2/hexane, collected by filtration, and vacuum dried to afford **3a** as an analytically pure tan powder (0.173 g, 0.224 mmol, 67%), mp 160–165 °C dec. Anal. Calcd for $C_{24}H_{23}BF_4INOPRe$: C, 37.32; H, 3.00. Found: C, 37.60; H, 2.99.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_3)]^+BF_4^-$ (3b). This compound was prepared from **1** (0.186 g, 0.333 mmol), CH_2Cl_2 (20 mL), HBF_4·Et_2O (0.045 mL, 0.35 mmol), and CH_3CH_2I (0.080 mL, 1.00 mmol) by a procedure analogous to that used to obtain **3a**. This gave **3b** as an analytically pure tan powder (0.183 g, 0.233 mmol, 70%), mp 145–150 °C dec. Anal. Calcd for $C_{25}H_{25}BF_4INOPRe$: C, 38.19; H, 3.20. Found: C, 38.58; H, 3.20.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2CH_3)]^+BF_4^-$ (3c). This compound was prepared from **1** (0.194 g, 0.347 mmol), HBF_4·Et_2O (0.044 mL, 0.35 mmol), and $CH_3CH_2CH_2I$ (0.135 mL, 1.38 mmol) by a procedure analogous to that used to obtain **3a** (75 mL of hexane was used to effect precipitation). This gave **3c** as an analytically pure tan powder (0.240 g, 0.300 mmol, 86%), mp 156–160 °C dec. Anal. Calcd for $C_{26}H_{27}BF_4INOPRe$: C, 39.02; H, 3.40. Found: C, 38.90; H, 3.46.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2CH_2CH_3)]^+BF_4^-$ (3d). This compound was prepared from **1** (0.229 g, 0.410 mmol), HBF_4·Et_2O (0.055 mL, 0.430 mmol), and $CH_3CH_2CH_2CH_2I$ (0.23 mL, 2.02 mmol) by a procedure analogous to that used to obtain **3a** (10 mL of CH_2Cl_2 solvent, 100 mL of hexane to effect precipitation). This gave **3d** as an analytically pure tan powder (0.266 g, 0.327 mmol, 80%), mp 149–152 °C dec. Anal. Calcd for $C_{27}H_{29}BF_4INOPRe$: C, 39.82; H, 3.59. Found: C, 39.52; H, 3.73.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-$·$(CH_2Cl_2)_{0.5}$[3e·$(CH_2Cl_2)_{0.5}$]. This compound was prepared from **1** (0.208 g, 0.372 mmol), HBF_4·Et_2O (0.050 mL, 0.395 mmol), and $(CH_3)_3SiCH_2I$ (0.275 mL, 1.85 mmol) by a procedure analogous to that used to obtain **3a**. This gave **3e**·$(CH_2Cl_2)_{0.5}$ as an analytically pure tan powder (0.287 g, 0.324 mmol, 87%), mp 144–147 °C dec. Anal. Calcd for $C_{27}H_{31}BF_4INOPRe$·$(CH_2Cl_2)_{0.5}$: C, 37.24; H, 3.64; Cl, 4.00. Found: C, 37.51; H, 3.77; Cl, 4.37. A sample was recrystallized from CH_2Cl_2/hexane to give **3e**·$(CH_2Cl_2)_{0.5}$ as small orange prisms: mp 144–147 °C dec; ^1H NMR (δ, $CDCl_3$) 5.28 (CH_2Cl_2, 0.5 H versus C_5H_5). Anal. Found (duplicate, two samples): C, 37.20, 37.48; H, 3.59, 3.61.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2CH_2Cl)]^+BF_4^-$ (3f). This compound was prepared from **1** (0.212 g, 0.380 mmol),

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$HBF_4{\cdot}Et_2O$ (0.052 mL, 0.41 mmol), and $ICH_2CH_2CH_2Cl$ (0.20 mL, 1.86 mmol) by a procedure analogous to that used to obtain **3a** (100 mL of ether was used to effect product precipitation). This gave **3f** as an analytically pure tan-brown powder (0.265 g, 0.317 mmol, 84%), mp 138–141 °C dec. Anal. Calcd for $C_{26}H_{26}BClF_4INOPRe$: C, 37.41; H, 3.14. Found: C, 37.52; H, 3.22.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Cl)]^+BF_4^-$ (3g). A Schlenk flask was charged with **1** (0.154 g, 0.276 mmol), CH_2Cl_2 (10 mL), ICH_2Cl (0.20 mL, 2.75 mmol), and a stir bar and was fitted with a septum. The orange solution was cooled to −78 °C and stirred. Then $HBF_4{\cdot}Et_2O$ (0.038 mL, 0.300 mmol) was added via syringe. The solution was allowed to warm to room temperature and was kept at room temperature for 0.5 h. Ether (100 mL) was added. A yellow powder precipitated, which was collected on a fine frit and dried under oil pump vacuum to give **3g** as an analytically pure golden yellow powder (0.143 g, 0.177 mmol, 64%), mp 139–140 °C dec. Anal. Calcd for $C_{24}H_{22}BClF_4INOPRe$: C, 35.73; H, 2.75. Found: C, 35.70; H, 2.50.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(IC_5H_5)]^+BF_4^-$ (3h). This compound was prepared from **1** (0.200 g, 0.358 mmol), C_6H_5I (0.40 mL, 3.57 mmol), and $HBF_4{\cdot}OEt_2$ (0.048 mL, 0.379 mmol) by a procedure analogous to that used to obtain **3g** (initial green color observed; 1 h reaction at room temperature). This gave **3h** as an analytically pure tan powder (0.196 g, 0.235 mmol, 66%), mp 147–150 °C dec. Anal. Calcd for $C_{29}H_{25}BF_4INOPRe$: C, 41.74; H, 3.02. Found: C, 41.90; H, 3.04.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(p\text{-}IC_6H_4OCH_3)]^+BF_4^-$ (3i). A Schlenk flask was charged with **1** (0.100 g, 0.179 mmol), CH_2Cl_2 (5 mL), p-$IC_6H_4OCH_3$ (0.166 g, 0.709 mmol), and a stir bar and was fitted with a septum. The solution was cooled to −78 °C and stirred. Then $HBF_4{\cdot}OEt_2$ (0.024 mL, 0.181 mmol) was added by syringe. The solution was allowed to warm to room temperature and was kept at room temperature for 0.5 h. Hexane (50 mL) was added, and an oil separated. Solvent was decanted, and the oil was dissolved in CH_2Cl_2. Hexane (50 mL) was added, and a tan powder precipitated. The powder was collected by filtration and again precipitated from CH_2Cl_2/hexane. The tan powder was collected on a medium frit and dried under oil pump vacuum to give **3i** (0.109 g, 0.126 mmol, 72%), mp 119–121 °C dec. Anal. Calcd for $C_{30}H_{27}BF_4INO_2PRe$: C, 41.68; H, 3.15. Found: C, 40.98; H, 3.55.

Thermal Decomposition of 3a–c. The following experiment is representative. A 5-mm NMR tube was charged with **3b** (0.0159 g, 0.0202 mmol), Ph_3SiCH_3 standard (0.0051 g, 0.0186 mmol), and CD_2Cl_2 (0.70 mL) and was capped with a septum. The tube was kept at room temperature, and ^1H and ^{31}P NMR spectra were periodically recorded. After 50 h, decomposition was complete to (yields by ^1H NMR integration vs standard) (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**6**; 0.0066 mmol, 65%), (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (**7**; 0.0028 mmol, 28%), and ICH_2CH_3 (0.0079 mmol, 39%).

Reactions of 3a–c with CH_3CN. The following experiment is representative. A 5-mm NMR tube was charged with **3b** (0.0252 g, 0.0320 mmol), Ph_3SiCH_3 standard (0.0082 g, 0.0299 mmol), and CD_2Cl_2 (0.70 mL) and was capped with a septum. Then CH_3CN (0.0032 mL, 0.061 mmol) was added via syringe. The tube was kept at 25 °C, and ^1H and ^{31}P NMR spectra were periodically recorded. After 24 h, reaction was complete to give (yields by ^1H NMR integration vs standard) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**8**;[21] 0.0272 mmol, 85%), ICH_2CH_3 (0.0237 mmol, 74%), and (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2X^+BF_4^-$ (**7**,**8**; 0.0014 mmol, 9%).

Reactions of 3a–c with Ph_3P and PPN^+Br^-. The following experiment is representative. A 5-mm NMR tube was charged with **3b** (0.0244 g, 0.0310 mmol), PPh_3 (0.0097 g, 0.0370 mmol), Ph_3SiCH_3 standard (0.0066 g, 0.0240 mmol), and $CDCl_3$ (0.70 mL) and was capped with a septum. Then ^1H and ^{31}P spectra were recorded within 0.25 h and showed the formation of (yields by ^1H NMR integration vs standard) $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**5**;[20] 0.029 mmol, 94%) and $Ph_3PCH_2CH_3^+BF_4^-$ (**9b**; 0.027 mmol, 87%) to be complete.

Reactions of Alkyl Iodides with Ph_3P. The following experiment is representative. A 5-mm NMR tube was charged with PPh_3 (0.0072 g, 0.028 mmol) and $CDCl_3$ (0.70 mL) and was capped with a septum. Then ICH_2CH_3 (0.0029 mL, 0.036 mmol) was added via syringe. The tube was kept at 25 °C, and after 18 h, a ^1H NMR spectrum indicated the reaction to be 9 ± 2% complete.

Rate Studies. Error analysis of linear regression data was carried out with the program StatView (BrainPower, Inc., Calabasas, CA); error limits correspond to one standard deviation. Probe temperatures were calibrated with methanol (<25 °C) and ethylene glycol (>25 °C). The following experiments are representative.

A 5-mm NMR tube was charged with **1** (0.0100 g, 0.0179 mmol) and capped with a septum. Then CD_2Cl_2 (0.70 mL) was added and the resulting solution cooled to −78 °C. Then $HBF_4{\cdot}Et_2O$ was added (0.0025 mL, 0.0197 mmol, 1.1 equiv) and the tube shaken at −78 °C to give **2-d_2**. Then CH_3I (0.011 mL, 0.177 mmol; purified by passage through alumina) was added ($[CH_3I] \simeq 0.25$ M). The sample was quickly transferred to a NMR probe that had been preequilibrated to −41.0 °C. Data acquisition was begun after a 7–10-min thermal equilibration period. The disappearance of **2-d_2** was monitored by integration of the cyclopentadienyl ^1H NMR resonance (δ 5.70 vs TMS). Standard analysis gave the rates in Table II.[22b]

A 5-mm NMR tube was charged with **3b** (0.0302 g, 0.0384 mmol) and PPh_3 (0.0203 g, 0.0774 mmol) and capped with a septum. The tube was cooled in a dry ice/$CHCl_3$ bath (−63 °C), and $CDCl_3$ (0.70 mL) was slowly added via syringe. The tube was quickly transferred to a NMR probe that had been preequilibrated to the desired temperature (218–243 K). The disappearance of **3b** was monitored by integration of the cyclopentadienyl ^1H NMR resonance, and the appearance of $Ph_3PCH_2CH_3^+BF_4^-$ was monitored by integration of the methyl ^1H NMR resonance. Standard analysis gave the rates in Table VI.[22b]

Preparation of $Ph_3PCH_2CH_2CH_3^+BF_4^-$ (9c). A round-bottom flask was charged with $Ph_3PCH_2CH_2CH_3^+Br^-$ (0.526 g, 1.36 mmol), $AgBF_4$ (0.280 g, 1.44 mmol), CH_3OH (25 mL), and a stir bar. The mixture was stirred for 0.25 h and was then poured through a 3-cm pad of Celite on a coarse glass frit. The volatiles were removed from the filtrate to give a white microcrystalline powder, which was recrystallized from CH_2Cl_2/hexane and dried under vacuum to give **9c** as clear, colorless needles (0.507 g, 1.29 mmol, 95%): mp 173–174 °C, IR (cm^{-1}, KBr) ν_{BF} 1106 (vs), 1050 (vs), 1043 (vs); ^1H NMR (δ, $CDCl_3$) 7.77–7.61 (m, 3 C_6H_5), 3.17 (m, PCH_2), 1.60 (pseudoseptet, J = 7.7 Hz, CCH_2C), 1.12 (dt, J_{HP} = 1.2 Hz, J_{HH} = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 135.07 (d, J_{CP} = 3.0 Hz, C_6H_5), 133.26 (d, J_{CP} = 9.9 Hz, C_6H_5), 130.46 (d, J_{CP} = 11.5 Hz, C_6H_5), 117.92 (d, J_{CP} = 86.2 Hz, C_6H_5), 23.55 (d, J_{CP} = 51.2 Hz, PCH_2), 16.33 (d, J_{CP} = 4.2 Hz, CH_2), 14.94 (d, J_{CP} = 17.6 Hz, CH_3); ^{31}P NMR (ppm, $CDCl_3$) 23.4 (s). Anal. Calcd for $C_{21}H_{22}BF_4P$: C, 64.31; H, 5.65. Found: C, 64.00; H, 5.21.

Preparations of $Ph_3PCH_3^+BF_4^-$ (9a) and $Ph_3PCH_2CH_3^+BF_4^-$ (9b). These known compounds were obtained as white powders by procedures analogous to those utilized to obtain **9c**, but omitting recrystallization (1.33–1.36 mmol scales, 98–99% yields). Data for **9a**: mp 129–131 °C (lit.[23a] mp 133–134 °C); IR (cm^{-1}, KBr) ν_{BF} 1055 (vs), 1040 (vs); ^1H NMR (δ, $CDCl_3$) 7.76–7.55 (m, 3 C_6H_5), 2.79 (d, J_{HP} = 13.4 Hz, CH_3); ^{13}C NMR (ppm, $CDCl_3$) 135.11 (d, J_{CP} = 3.0 Hz, C_6H_5), 132.92 (d, J_{CP} = 10.6 Hz, C_6H_5), 130.38 (d, J_{CP} = 13.0 Hz, C_6H_5), 118.81 (d, J_{CP} = 88.8 Hz, C_6H_5), 8.82 (d, J_{CP} = 58.7 Hz, CH_3); ^{31}P NMR (ppm, $CDCl_3$) 21.3 (s). Data for **9b**: mp 128–131 °C (lit.[23b] 127 °C); IR (cm^{-1}, KBr) ν_{BF} 1116 (vs), 1054 (vs), 1042 (vs); ^1H NMR (δ, $CDCl_3$) 7.78–7.61 (m, 3 C_6H_5), 3.25 (dq, J_{HP} = 12.5 Hz, J_{HH} = 7.5 Hz, PCH_2), 1.31 (dt, J_{HP} = 19.9 Hz, J_{HH} = 7.5 Hz, CH_3); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 135.01 (d, J_{CP} = 3.0 Hz, C_6H_5), 133.21 (d, J_{CP} = 9.8 Hz, C_6H_5), 130.40 (d, J_{CP} = 12.5 Hz, C_6H_5), 117.61 (d, J_{CP} = 86.0 Hz, C_6H_5), 16.02 (d, J_{CP} = 53.0 Hz, CH_2), 6.60 (d, J = 5.3 Hz, CH_3); $^{31}P\{^1H\}$ (ppm, $CDCl_3$) 25.7 (s).

X-ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-{\cdot}(CH_2Cl_2)_{0.5}$ [3e·$(CH_2Cl_2)_{0.5}$]. Data were collected as described in Table III. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 15 reflections in the range $22° < 2\theta < 28°$. There were no systematic absences, and the space group was determined to be $P\bar{1}$ (No. 2).

A total of 5140 reflections were collected. As a check on crystal stability, two representative reflections were measured every 97 reflections. The slope of the least-squares line through a plot of intensity vs time was −81 ± 4 counts/h. An anisotropic decay correction was applied, with correction factors I ranging from 0.974 to 1.262 (average 1.091). Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ϕ scans, were applied to the data. Intensities of equivalent reflections were averaged, and two reflections were rejected because their intensities differed significantly from the average. The agreement factors for the averaging of the 546 observed and accepted reflections were 2.2% based upon intensity and 1.4% based upon F_o.

The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - F_c|)^2$, with a unit weight for all observed reflections. All non-hydrogen atoms, with the exception of those in the disordered CH_2Cl_2 molecule, were refined with anisotropic thermal parameters. Scattering factors, and values for $\Delta f'$ and $\Delta f''$, were taken from the literature.[37] Anomalous dispersion effects were included in F_c.[38] All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[39]

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X-ray Crystal Structure of (η^5-$C_5H_4CH_3$)Re(NO)(PPh_3)(I) (4). Irregular deep red prisms of **4**[14] were obtained by recrystallization from CH_2Cl_2/hexane. Data were collected as described in Table III. Cell constants and an orientation matrix were obtained from least-squares refinement, using the setting angles of 15 reflections in the range 20° < 2θ < 26°. The space group was determined from the systematic absences ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $k = 2n$) and subsequent least-squares refinement.

A total of 2645 reflections were collected. Corrections were applied and the structure was solved as described for **3e**·$(CH_2Cl_2)_{0.5}$ above. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized positions.

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for iodide complex **4** (2 pages); calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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Arene-Metal-Carborane Triple-Decker Sandwiches. Designed Synthesis of Homo- and Heterobimetallic Complexes of Cobalt, Iron, Ruthenium, and Osmium[1]

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Abstract: This paper describes the systematic preparation and characterization of new families of triple-decker sandwich complexes incorporating formal *cyclo*-$Et_2C_2B_3H_3^{4-}$ bridging ligands, including the first species of this class containing second- or third-row transition metals. Complexes of general formula (L)M($Et_2C_2B_3H_3$)M'(L) (M = Ru, Os; M' = Co, Ru; L = cymene [*p*-isopropyltoluene], Cp, or C_5Me_5) were obtained in stepwise fashion via (1) synthesis of *closo*-(L)M($Et_2C_2B_4H_4$) metallacarboranes, (2) "decapitation" (apex BH removal) of these complexes to give *nido*-(L)M($Et_2C_2B_3H_5$), (3) bridge deprotonation to form the corresponding mono- or dianion, and (4) reaction of the anion with an arene metal halide to generate the desired triple-decker compound. In addition, the cobalt-iron triple-decker CpCo($Et_2C_2B_3H_3$)FeCp was prepared via treatment of (η^6-C_8H_{10})Fe($Et_2C_2B_3H_4$)$^-$ with Na^+Cp^- and $CoCl_2$ followed by air oxidation. The reaction of $(CO)_3RuCl_2$ with (C_5Me_5)-Co($Et_2C_2B_3H_3$)$^{2-}$ gave the "pseudo-triple-decker" complex (C_5Me_5)Co($Et_2C_2B_3H_3$)Ru$(CO)_3$. The triple-deckers, especially those containing osmium, are susceptible to chlorination by $RuCl_3$, $OsCl_3$, or dichloromethane, forming exclusively the 4-chloro derivatives. All of the characterized triple-decker complexes are air-stable crystalline solids (except for the osmium-ruthenium species, which are air sensitive) and have been structurally characterized from their ^{11}B and ^1H NMR, infrared, visible-UV, and unit- and high-resolution mass spectra, further supported by X-ray crystallographic analyses of (cymene)Ru-($Et_2C_2B_3H_3$)Ru(cymene) (**10**) and CpCo($Et_2C_2B_3H_3$)Ru(cymene) (**11a**). Crystal data for **10**: mol wt 561.13; space group $P\bar{1}$; $Z = 2$; a = 10,409 (3), b = 11.268 (5), c = 12.002 (4) Å; α = 96.16 (3), β = 99.49 (2), γ = 106.69 (3)°; V = 1312 (2) Å^3; R = 0.043 for 4777 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **11a**: mol wt 476.92; space group $P2_1/c$; $Z = 4$; a = 8.808 (6), b = 17.708 (8), c = 14.194 (8) Å; β = 103.50 (4)°; V = 2153 (4) Å^3; R = 0.058 for 3289 reflections having $F_o^2 > 3\sigma(F_o^2)$.

A primary goal in our research is the tailored synthesis of electron-delocalized organometallic oligomers and polymers, and our overall strategy entails the construction of progressively larger polymetallic systems via systematic, controlled methods.[2] The ultimate objective is to develop preparative routes to substances having specified structure-correlated properties (e,g., conducting polymers) via the assembly of selected metals and ligands. In earlier work we demonstrated[1-3] that arene and small carborane ligands, in combination with transition metals, form stable, robust complexes that are amenable to chemical modification and in some cases exhibit reversible electrochemical changes in metal oxidation states;[4] moreover, reasonably general syntheses of such complexes, and their small *nido*-carborane precursors, are now available.[2]

In our approach, B- and C-substituted derivatives of the *nido*-2,3-dicarbahexaborane $C_2B_4H_8$ are bridge deprotonated, η^5-coordinated to transition metals to create metallacarborane clusters, and subsequently incorporated into larger carborane-metal-arene systems that are stabilized by the carborane units. In recent publications we have described synthetic routes to mono-, bis- and tris(carboranyl) derivatives that have been specifically tailored as ligands for this purpose and have aryl, polaryl, or alkyl substituents.[5] With these materials in hand, we have undertaken to develop methods for converting them into arene-metal-carborane double- and triple-decker sandwich complexes incorporating

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