Site-selective oxidative-addition reactions in a heterometallic octanuclear carbido cluster compound. A reactivity parallel with mononuclear indenyliridium complexes

Linqing. Ma, Lawrence P. Szajek, and John R. Shapley

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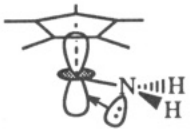
$$1 \xrightarrow{2NH_3} \underset{80\%\ \text{yield}}{[ReCp^*Me_3(NH_3)_2]^+OTf^-\ (4)} \xrightarrow[\substack{-NEt_3\cdot HOTf \\ -NH_3}]{NEt_3} \underset{70\%\ \text{yield}}{ReCp^*Me_3(NH_2)\ (5)} \quad (2)$$

are equivalent in pseudooctahedral **4** or (less likely) that they are exchanging rapidly on the NMR time scale, even at −95 °C. If the former explanation is correct then the structure would not be analogous to that known for $[WCp^*Me_3(\eta^2\text{-}N_2H_4)]OTf$.[1] The amido protons in **5** at −80 °C are equivalent. They would be inequivalent if the lone pair on nitrogen were donated into an empty orbital ($\sim d_{xy}$) that points between the ligands in a square pyramid.[10] Perhaps the d_{xy} orbital contains the two d electrons and the lone pair is donated into what is approximately a d_{z^2} orbital, viz.



It is also possible that the π bond is especially weak, regardless of how it is formed, and rotation about the Re–N bond therefore rapid on the NMR time scale under all conditions employed. Addition of triflic acid to **5** in ether yields $[ReCp^*Me_3(NH_3)]OTf$ (**6**).[11] The proton NMR spectrum of **6** in CD_2Cl_2 shows an unusual temperature-dependent paramagnetic contribution to the chemical shifts, a situation related to that noted above for **1**; resonances are found (at 20 °C in CD_2Cl_2) at 16.02 (Me), 14.60 (2 Me), 10.20 (NH_3), and 2.15 ppm (Cp*) and (at −80 °C) at 5.00 (NH_3), 4.30 (Me), 2.90 (2 Me), and 1.70 ppm (Cp*).

Reduction of **2** by 87% zinc amalgam in the presence of 2,6-lutidine hydrochloride in THF reproducibly yields 1.20 equiv of ammonia. Reduction of **2** using 0.5% sodium amalgam (in the presence of lut·HCl) produced 1.46 equiv of ammonia, while reduction using zinc amalgam in the absence of protons produced 1.00 equiv of ammonia. These experiments suggest that the N–N bond can be cleaved in neutral d^3 $ReCp^*Me_3(NH_2NH_2)$ but that the resulting $ReCp^*Me_3(NH)$ is not efficiently protonated and reduced to give the second equivalent of ammonia under conditions employed so far.

We conclude that high-oxidation complexes containing the $ReCp^*Me_3$ core and NH_x or N_2H_y ligands are reasonably stable and that N–N bond cleavage in $ReCp^*Me_3(NH_2NH_2)$ may be a controlled reaction, as it is in $MCp^*Me_3(\eta^2\text{-}NH_2NH_2)$ (M = Mo, W).[1] Future studies will be aimed at expanding chemistry that is relevant to the reduction of dinitrogen and comparing and contrasting it with analogous chemistry of complexes containing the MCp^*Me_3 core where M = Mo or W.[1,7,12]

Acknowledgment. R.R.S. thanks the National Institutes of Health for support through Grant GM 31978, and M.G.V. thanks the National Science Foundation for a predoctoral fellowship and C.C. Cummins for valuable discussions.

Supplementary Material Available: Textual description of syntheses, IR and NMR data, and analytical data (3 pages). Ordering information is given on any current masthead page.

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[10] Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

[11] $ReCp^*Me_3(NH_2)$ (0.150 g, 0.392 mmol) was dissolved in 10 mL of ether at −40 °C. Triflic acid (0.035 mL, 0.392 mmol) was added directly to the stirred dark green solution. A yellow precipitate formed immediately. After 10 min the yellow solid was filtered off, washed with ether, and dried in vacuo; yield 0.125 g (0.230 mmol, 60%).

[12] O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331. (c) Schrock, R. R.; Kolodzieg, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

Site-Selective Oxidative-Addition Reactions in a Heterometallic Octanuclear Carbido Cluster Compound. A Reactivity Parallel with Mononuclear Indenyliridium Complexes

Linqing Ma, Lawrence P. Szajek, and John R. Shapley*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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Summary: The reactions of triphenylsilane and allyl bromide with $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ in refluxing THF afforded products in which the substrates were added selectively to the iridium center. The products $[PPN]_2[Re_7C(CO)_{21}Ir(H)(CO)(SiPh_3)]$ (**1**) (77%) and $[PPN][Re_7C(CO)_{21}Ir(\eta^3\text{-}C_3H_5(CO)]$ (**2**) (40%) were characterized by analytical and spectroscopic data. The analogous reactions in refluxing cyclohexane with the indenyl complex $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ yielded $(\eta^5\text{-}C_9H_7)Ir(H)(CO)(SiPh_3)$ (**3**) (78%) and $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (**4**) (86%), respectively, which were similarly characterized. No reactions with the cyclopentadienyl complex $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ were observed under similar or more severe conditions.

There is an isolobal analogy between the cyclopentadienide ion and a triangular face of a polyhedral metal cluster in terms of their coordination by a metal complex fragment.[1] Motivated by this concept, we have prepared compounds of the formula $[Re_7C(CO)_{21}ML_n]^{2-}$,[2] which are complexes between the metal fragments $[ML_n]^+$ and the carbide cluster compound $[Re_7C(CO)_{21}]^{3-}$,[3] that

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[1] (a) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Grimes, R. N., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1990. (b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

[2] (a) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729. (b) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441. (c) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551. (d) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.

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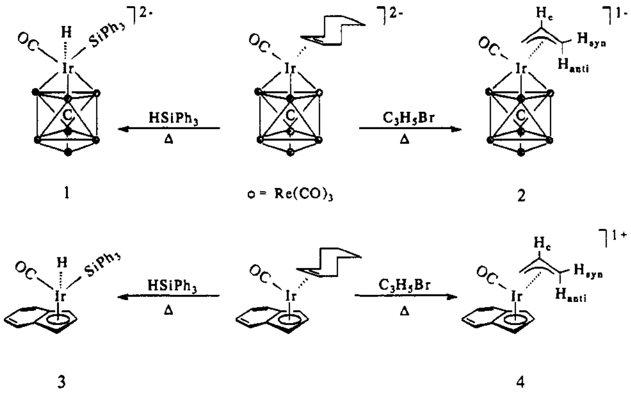
Scheme I



are compositional analogues of the complexes CpML$_n$. In view of the developments in oxidative-addition chemistry shown by CpIr centers,[4] we have specifically targeted an iridium complex, i.e., [Re$_7$C(CO)$_{21}$IrLL']$^{2-}$, that could undergo oxidative-addition reactions. Increasing attention has been paid to oxidative-addition reactions with binuclear and polynuclear compounds in recent years,[5] although such reactions involving high-nuclearity metal clusters are relatively rare.[6] Furthermore, recent studies of site selectivity in high-nuclearity mixed-metal clusters have not been extended past tetranuclear compounds.[9] We wish to report that the octanuclear compound [Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)]$^{2-}$ [14] undergoes oxidative-addition processes selectively at the iridium center. Intriguingly, however, the *reactivity* of this cluster complex more closely parallels that of the corresponding indenyl complex (η^5-C$_9$H$_7$)Ir(C$_8$H$_7$)Ir(C$_8$H$_{14}$)(CO)[15] (see Scheme I) than that of the cyclopentadienyl complex (η^5-C$_5$H$_5$)Ir(C$_8$H$_{14}$)(CO).[15]

When [A]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)], where A$^+$ = PPN$^+$ or Et$_4$N$^+$, was allowed to react with HSiPh$_3$ in refluxing THF, the oxidative-addition product [A]$_2$[Re$_7$C(CO)$_{21}$Ir(H)(CO)(SiPh$_3$)] (A$^+$ = PPN$^+$ (**1a**), Et$_4$N$^+$ (**1b**)) was isolated as a black solid. The formulation is based on analytical and mass spectral results as well as on ^{1}H and ^{13}C NMR data.[16] In the ^{13}C NMR spectrum of **1a** when no broad-band decoupling was applied, only the carbonyl resonance at δ 174.0 showed a small coupling of 4.6 Hz, which was confirmed as due to the hydride ligand by a selective ^{1}H-decoupling experiment. On the basis of its relative intensity and chemical shift, this carbon resonance is assigned to the single carbonyl bound to iridium, and since no other coupling was observed in the ^{13}C NMR spectrum, the hydride ligand must also be bonded only to the iridium center. The question of possibly incomplete H–Si bond oxidative addition, which is frequently encountered in mononuclear systems,[17] was also addressed. In that regard, under the experimental conditions (S/N > 200) that should allow the observation of ^{29}Si satellites in the ^{1}H NMR spectrum, no ^{29}Si–^{1}H coupling was observed that was larger than the line width at the base of the hydride signal ($J_{\text{Si-H}} < 16$ Hz). This fact strongly implies complete oxidative addition of the H–Si bond in **1**.[17]

The reaction of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)] with allyl bromide also gave a product due to an overall oxidative addition, and [PPN][Re$_7$C(CO)$_{21}$Ir(η^3-C$_3$H$_5$)(CO)] (**2**) was isolated as a black solid.[18] The ^{13}C NMR carbonyl resonances of **2** all shift to higher field compared to those of the starting cluster compound, in agreement with the charge reduction. The ^{1}H NMR spectrum of **2** shows the allyl ligand adopts an η^3-coordination mode. ^{13}C NMR further shows that the η^3-allyl group must coordinate only to the iridium center, since the typical[2b,3a] 3:9:9 pattern of carbonyl resonances for the (μ_6-C)[Re(CO)$_3$]$_7$ moiety is observed. This allyl coordination mode is similar to that in [Ph$_4$P][Rh$_6$(CO)$_{14}$(η^3-C$_3$H$_5$)],[19] but it is different from the bridging mode reported for the carbido cluster [PPN][Ru$_6$C(CO)$_{15}$(μ_2,η^3-C$_3$H$_5$)].[8]

The indenyl iridium complex (η^5-C$_9$H$_7$)Ir(C$_8$H$_{14}$)(CO)[15] reacts cleanly with triphenylsilane in refluxing cyclohexane to form (η^5-C$_9$H$_7$)Ir(H)(CO)(SiPh$_3$) (**3**).[20,21] Again, by ^{1}H

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(3) (a) Hayward, C.-M. T.; Shapley, J. R. *Organometallics*, **1988**, *7*, 448. (b) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339.

(4) (a) Dziallas, H.; Höhn, A.; Werner, H. *J. Organomet. Chem.* **1987**, *330*, 207. (b) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *12*, 2653, 2658. (c) Bergman, R. G. *J. Organomet. Chem.* **1990**, *400*, 273. (d) Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81. (e) Ricci, J. S.; Koetzle, T. F.; Fernandez, M.-J.; Maitlis, P. M.; Green, J. *Organomet. Chem.* **1986**, *383*, 299. (f) Jones, W. D. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley and Sons: New York, 1989; Chapter 4.

(5) Bradley, J. S. In *Metal Clusters*; Moskovits, M., Ed.; John Wiley and Sons: New York, 1986; Chapter 5. (b) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 5. (c) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 7.

(6) Among the few reported examples are the reactions of the iron triad M$_5$C(CO)$_{15}$ (M = Ru, Os) compounds with H$_2$ and HX (X = Cl, Br, I, SEt, SH, SeH)[7] and the recently reported reactions of methyl iodide and allyl bromide with [PPN]$_2$[Ru$_6$C(CO)$_{16}$].[8]

(7) Vargas, M. D.; Nicholls, J. D. *Adv. Inorg. Radiochem.* **1986**, *30*, 123.

(8) Chihara, T.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1990**, *383*, 367.

(9) Examples of small cluster systems showing metal specificity in ligand substitution have been described for various trinuclear and tetranuclear compounds,[10-12] and an example of selective oxidative addition of H$_2$ at the ruthenium centers of Ru$_2$Co$_2$(CO)$_{13}$ has been reported.[13]

(10) Atwood, J. D.; Sojaie, R. *Inorg. Chem.* **1987**, *26*, 2199; 1988, *27*, 2558.

(11) Keister, J. B.; Onyeso, C. C. O. *Organometallics* **1988**, *7*, 2364.

(12) Bantel, H.; Bernhardt, W.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1988**, *121*, 1247.

(13) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 183.

(14) Ma, L.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 5133.

(15) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357. The preparation of (η^5-C$_5$H$_5$)Ir(C$_8$H$_{14}$)(CO) was analogous to that of (η^5-C$_9$H$_7$)Ir(C$_8$H$_{14}$)(CO), starting from [Ir(C$_8$H$_{14}$)$_2$(CO)Cl]$_2$ and TlCp.

(16) A THF solution of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)] (53 mg, 0.016 mmol) and HSiPh$_3$ (6.4 mg, 0.025 mmol) was heated to reflux for 4 h. The solvent was removed in vacuo, and the residue was crystallized from dichloromethane/2-propanol by solvent diffusion. [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(H)(CO)(SiPh$_3$)] (**1a**) was isolated as a black microcrystalline solid (42 mg, 77%). Spectroscopic data for **1a** are as follows. IR (acetone): ν_{CO} 2053 (w), 2043 (vw), 2003 (vs), 1983 (w, sh), 1946 (w), 1926 (w), 1889 cm^{-1} (vw). ^{1}H NMR (acetone-d_6, 20 °C): δ 8.00–7.20 (m, 75 H, *H* of C$_6$H$_5$), 15.70 (s, 1 H, Ir–*H*). ^{13}C NMR (CD$_2$Cl$_2$, 0 °C): δ 204.1 (s, 3 C), 192.1 (s, 9 C), 191.0 (s, 9 C), 174.0 (d, 1 C, $^2J_{\text{CH}}$ = 4.6 Hz, Ir–*C*O). FAB-MS (negative ion) (^{187}Re, ^{193}Ir): m/z 2928 (M – PPN). However, **1a** did not give satisfactory elemental analysis results, and [Et$_4$N]$_2$[Re$_7$C(CO)$_{21}$Ir(H)(CO)(SiPh$_3$)] (**1b**) was used for this purpose. Anal. Calcd for C$_{57}$H$_{56}$N$_2$IrO$_{22}$Re$_7$Si: C, 25.89; H, 2.13; N, 1.06. Found: C, 25.71; H, 1.95; N, 1.01.

(17) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

(18) A THF solution of [PPN]$_2$[Re$_7$C(CO)$_{21}$Ir(C$_8$H$_{14}$)(CO)] (95 mg, 0.029 mmol) and allyl bromide (5.0 mL, 0.058 mmol) was heated to reflux for 2 h. The reaction mixture was chromatographed on a deactivated neutral alumina column with dichloromethane. A purple band was eluted first, from which [PPN][Re$_7$C(CO)$_{21}$Ir(η^3-C$_3$H$_5$)(CO)] (**2**) was isolated after crystallization from chloroform/pentane by layering (33 mg, 40%). Anal. Calcd for C$_{63}$H$_{36}$Cl$_3$NIrO$_{22}$P$_2$Re$_7$([PPN][Re$_7$C(CO)$_{21}$Ir(η^3-C$_3$H$_5$)(CO)]·CHCl$_3$): C, 26.80; H, 1.29; N, 0.50; Cl, 3.77. Found: C, 27.07; H, 1.38; N, 0.44; Cl, 3.93. IR (acetone): ν_{CO} 2066 (w), 2026 (m), 2014 (vs), 1989 (w), 1965 (w), 1942 (w), 1896 cm^{-1} (vw). ^{1}H NMR: δ 7.80–7.40 (m, C$_6$H$_5$), 5.49 (m, 1 H, H$_c$, J(H$_c$, H$_{\text{anti}}$) = 11.0 Hz, J(H$_c$, H$_{\text{syn}}$) = 6.3 Hz, J_{gem} not resolved), 3.49 (d, 2 H, H$_{\text{syn}}$), 3.10 (d, 2 H, H$_{\text{anti}}$). ^{13}C NMR (CDCl$_3$, 20 °C): δ 200.5 (s, 3 C), 188.8 (s, 9 C), 188.0 (s, 9 C), 158.6 (s, 1 C, Ir–*C*O). FAB-MS (negative ion) (^{187}Re, ^{193}Ir): m/z 2171 (M – PPN).

(19) Ciani, G.; Sironi, A.; Chini, P.; Ceriotti, A.; Martinengo, S. *J. Organomet. Chem.* **1980**, *192*, C39.

NMR spectroscopy, the Si–H bond is inferred to be completely cleaved,[22] and the ^{13}C NMR carbonyl resonance at δ 168.1 is coupled by 8.0 Hz to the hydride ligand. The fact that 3 is a chiral molecule is shown dramatically by the inequivalent ^1H NMR resonances of the indenyl ring. An analogous oxidative-addition reaction occurs with allyl bromide to provide $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (4).[23] The η^3-coordination mode is fully supported by the ^1H NMR data, and the downfield position of the central proton resonance suggests an exo configuration for the allyl ligand.[24] The cyclopentadienyl complex $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ does not react with either triphenylsilane or allyl bromide under the same or even more vigorous conditions.[25]

Examples of an "indenyl effect" that contributes to enhanced reactivity of indenyl complexes compared to cyclopentadienyl complexes are well documented, and it has been generally supposed that an η^5-to-η^3 slip of the indenyl ring facilitates attack by the incoming reagents.[26] In particular, this idea has been invoked to account for the facile reactions of $(\eta^5\text{-}C_9H_7)Ir(PPh_3)_2$ with organic halides to form oxidative-addition products.[27] Since both $[PPN]_2[Re_7C(CO)_{21}Ir(C_8H_{14})(CO)]$ and $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ also undergo substitution of the cyclooctene ligand, e.g., by ethylene,[14,15] more rapidly than does $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$, a "slip mechanism" may be operating for both reactive compounds. However, it is not clear in general whether the indenyl ring slip occurs before or after the reactants come together, and a similar driving force is not obvious for the cluster compound. Thus, details of the reaction profiles remain to be established.

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(20) $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ (65 mg, 0.15 mmol) and triphenylsilane (38 mg, 0.15 mmol) were heated to reflux in cyclohexane for 5 h. The solvent was removed under reduced pressure, and the orange oily residue was chromatographed with diethyl ether on a column of activated neutral alumina. The orange band was collected, reduced in volume to ca. 1 mL, and left at −20 °C. After 1 week dark yellow crystals of $(\eta^5\text{-}C_9H_7)Ir(H)(CO)(SiPh_3)$ (3) were isolated (69 mg, 78%). Mp (sealed tube): 119 °C. Anal. Calcd for $C_{28}H_{23}IrOSi$: C, 56.36; H, 3.89. Found: C, 56.63; H, 3.87. IR (cyclohexane): ν_{CO} 2011 cm^{-1}. IR (KBr): ν_{CO} 1982, ν_{Ir-H} 2145 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): 7.32–7.52 (m, 15 H, C_6H_5), 7.46 (m, 1 H, C_9H_7), 7.42 (m, 1 H, C_9H_7), 7.20 (m, 2 H, C_9H_7), 6.09 (br, 1 H, C_9H_7), 5.25 (t, 1 H, C_9H_7), 4.97 (br, 1 H, C_9H_7), 15.91 (s, 1 H, Ir–*H*). FD-MS (150 °C, 70 eV) (^{193}Ir): m/z 596 (M^+).

(21) This compound was mentioned in an article by Graham[4d] as the product from treatment of $(\eta^5\text{-}C_9H_7)Ir(CO)_2$ with triphenylsilane. No experimental details were given.

(22) The only other example of silane oxidative addition with a Cp-analogue iridium(I) complex of which we are aware is the recent report by Crabtree (Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415) that $(triso)Ir(C_2H_4)_2$, where triso = $C\{Ph_2P{=}O\}_3$, reacts with $HSiPh_3$ to give $(triso)Ir(C_2H_4)(H)(SiPh_3)$.

(23) A cyclohexane solution of $(\eta^5\text{-}C_9H_7)Ir(C_8H_{14})(CO)$ (50 mg, 0.11 mmol) and allyl bromide (60 mL, 0.60 mmol) was heated to reflux for 4 h and then cooled to ambient temperature. The same work up as above was used. Dark orange crystals of $[(\eta^5\text{-}C_9H_7)Ir(\eta^3\text{-}C_3H_5)(CO)]Br$ (4) were isolated (43 mg, 86%). Anal. Calcd for $C_{13}H_{12}IrBrO$: C, 34.42; H, 2.65. Found: C, 34.08; H, 2.59. IR (cyclohexane): ν_{CO} 2054 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.46 (m, 2 H, C_9H_7), 7.34 (m, 2 H, C_9H_7), 5.69 (d, 2 H, C_9H_7), 5.65 (t, 1 H, C_9H_7), 5.14 (m, 1 H, H_c, $J(H_c, H_{anti})$ = 9.9 Hz, $J(H_c, H_{syn})$ = 6.3 Hz), 3.92 (dd, 2 H, H_{syn}, $J(H_{syn}, H_{anti})$ = 0.6 Hz), 2.37 (dd, 2 H, H_{anti}). FD-MS (150 °C, 70 eV) (^{193}Ir): m/z 459 (M^+).

(24) Wakefield, J. B.; Stryker, J. M. *Organometallics* **1990**, *9*, 2428.

(25) Bright yellow cyclohexane solutions of $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ (20 mg, 0.05 mmol) and either allyl bromide (30 mL, 0.30 mmol) or $HSiPh_3$ (15 mg, 0.05 mmol) were heated to reflux for 24 h. The carbonyl region of the IR spectrum showed no indication of reaction; i.e., only the absorption bands for $(\eta^5\text{-}C_5H_5)Ir(C_8H_{14})(CO)$ were observed. The solvent was removed under vacuum, and toluene (20 mL) was added. The solutions were heated to reflux for 24 h, but again no reaction was indicated by IR spectroscopy.

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