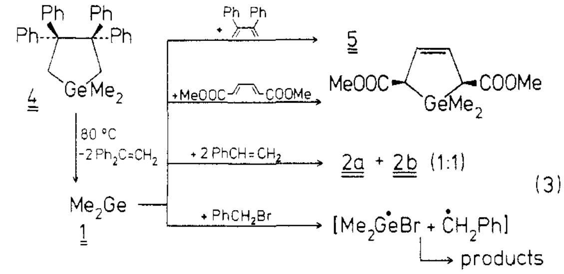
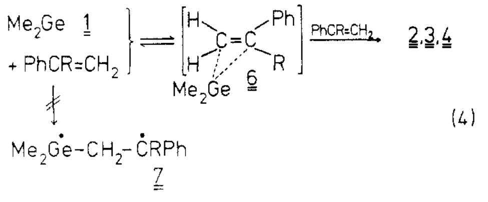


ration of (*Z*)-stilbene remained unchanged, thus proving the absence of an transient, reversible addition reaction.

Clearly, a regiospecific but not stereospecific reaction of dimethylgermylene with 2 mol of the olefin takes place, presumably involving a short-lived 1:1 intermediate. All considerations concerning the mechanism have to take into account the competing, very rapid polymerization of **1**, giving $(Me_3Ge)_n$ which is diffusion controlled, $k \approx 10^9$ M^{-1} s^{-1}. Hence, only very rapid reactions with an olefin can compete. For this to be the case, two requirements are apparent: (a) An terminal olefin must be used. Whereas α-methylstyrene reacts, β-methylstyrene does not. 1,1-Diphenylethylene reacts readily but the two isomeric stilbenes do not. This suggests an unsymmetrical transition state (or π complex) **6** of a type which is known for the approach of a free radical toward an olefin.[11] This is in accordance with our earlier observation[1b] that terminal conjugated dienes react faster (giving cheletropic cycloadditions) than do nonterminal dienes. Thus 2,3-diphenyl-1,3-butadiene is more reactive than 1,4-diphenyl-1,3-butadiene. (b) The other end of the olefin has to be substituted by at least one aromatic ring.[12] All of the other olefins tested did not react rapidly enough under similar conditions to compete successfully with the polymerization of **1**. This stabilizing effect of the Ph group cannot involve the stabilization of a free benzyl radical **7**, because in this case polystyrene should be observed, and the *t*-BuBr added to the mixture should capture the Ge-centered radical. However, this is not observed. Whatever the nature of the 1:1 intermediate **6**—a question to be cleared up in more detailed investigations—it should have one stronger C–Ge bond, the CH_2–Ge bond, and one weaker, the benzyl–C bond, ready for the insertion of the second molecule of olefin, as indicated in eq 4, thus causing the regiospecificity of the overall reaction.[13]



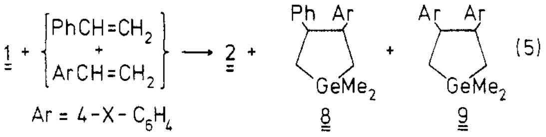
In a competition experiment, 2,3-diphenyl-1,3-butadiene undergoes a 1:1 reaction with **1** in the presence of an excess of styrene giving exclusively **5** (^1H NMR). Therefore, the cycloaddition is at least 10 times faster than the reaction with styrene. This could be an additional hint favoring the two-step mechanism of styrene, to be elucidated in the future.

Table I. Results of Competition Experiments with 1:1 Mixtures of Styrene and 4-X-Styrenes[a]

X	2	8	9
COMe	5	50	45
Cl	19	53	28
Me	26	51	24
OMe	30	52	18

[a] 2.0 mmol each + 0.6-mmol precursor of **1** in 5 mL of benzene at 80 °C. Total yields >80%; the relative distribution (SLC peak areas in percent, 2-m SE 30) is given.

In competition experiments with 1:1 mixtures of styrene and 4-X-styrenes, we found a rate sequence X = Me_2N (no yield) < OMe < Me ≈ H ≈ Cl < COMe with increasing yields of **8** and **9** (eq 5; Table I). Dimethylgermylene



exhibits, therefore, *nucleophilic* behavior in these cycloadditions with styrenes, as it does toward conjugated dienes.[1b]

Acknowledgment. This work has been supported by the Minister für Wissenschaft und Forschung, Düsseldorf, and the Fonds der Chemischen Industrie.

Registry No. **1**, 74963-95-4; **2a**, 94070-43-6; **2b**, 94070-44-7; **3a**, 94070-45-8; **3b**, 94070-46-9; **4**, 94070-47-0; **5**, 94070-48-1; 4-$COMeC_6H_4CH{=}CH_2$, 10537-63-0; 4-$ClC_6H_4CH{=}CH_2$, 1073-67-2; 4-$MeC_6H_4CH{=}CH_2$, 622-97-9; 4-$OMeC_6H_4CH{=}CH_2$, 637-69-4; Me_2GeCl_2, 1529-48-2; GeI_2, 13573-08-5; Styrene, 100-42-5; α-methylstyrene, 98-83-9; 1,1-diphenylethylene, 530-48-3; cyclohexene, 110-83-8; 1-phenylcyclopentene, 825-54-7; 3-phenylpropene, 300-57-2; 4,4-dimethylpentene, 762-62-9; (*E*)-β-methylstyrene, 873-66-5; (*E*)-Stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; *cis*-2,5-diphenylgermacyclopentane, 26436-21-5; *trans*-2,5-diphenylgermacyclopentane, 26436-22-6; 7,7-dimethyl-7-germanorbornadiene, 76054-64-3; *cis*-3,4-diphenylsilacyclopentane, 94070-49-2; *trans*-3,4-diphenylsilacyclopentane, 88296-43-9; *iso*-2,5-diphenylsilacyclopentane, 26436-15-7; *trans*-2,5-diphenylsilacyclopentane, 26436-16-8; 2,3-diphenylbutadiene, 2548-47-2; 3,4-dimethyl-1,1-diiodo-1-germacyclopent-3-ene, 94234-81-8.

---

(11) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753 and literature cited there.

(12) Other stabilizing groups such as CN or COOR in acrylic acid derivatives lead to other reactions outside the scope of this communication (work in progress).

(13) With a Si analogue, the isolated 1,1,2,2,3,3-hexamethylsilirane, a nonregiospecific two-atom insertion of styrene has been found, giving a mixture of 2-phenyl- and 3-phenylsilacyclopentanes. Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574. Earlier work is cited there.

Carbonylation of Metal–Oxygen Bonds. Formation of Carbalkoxydicarbonylbis(triphenylphosphine)iridium, $ROC(O)Ir(CO)_2(PPh_3)_2$, by Carbonylation of *trans*-Alkoxycarbonylbis(triphenylphosphine)iridium, *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, *n*-Pr, Ph)

Wayne M. Rees and Jim D. Atwood*[†]

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received September 5, 1984

Summary: Carbonylation of the complexes *trans*-$MeOIr(CO)(PPh_3)_2$, *trans*-(*n*-PrO)$Ir(CO)(PPh_3)_2$, and *trans*-$PhOIr(CO)(PPh_3)_2$ leads to carboalkoxy complexes $ROC(O)Ir(CO)_2(PPh_3)_2$ in high yield. Identification of the intermediate $Ir(CO)_3(PPh_3)_2^+$ OR^- indicates a two-step mechanism—first displacement of the alkoxide from the coordination sphere and then nucleophilic attack on a carbon of the cationic carbonyl complex. The hydroxy complex did not undergo carbonylation under similar conditions.

0276-7333/85/2304-0402$01.50/0

Carbonylation reactions are important in catalytic reactions such as hydroformylation and methanol homologation and will grow in importance with the shift toward synthesis gas as a feedstock. Alkyl migration, carbonylation of a transition metal–alkyl bond, has been frequently examined and is well understood.[1-14] Carbonylation of other types of metal–ligand bonds has not been studied as frequently and is not as well understood.[15] This communication reports the results of the carbonylation of *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, *n*-Pr, Ph), showing that the reaction proceeds by alkoxide attack on CO of the cationic species $Ir(CO)_3(PPh_3)_2^+$.

The use of palladium catalysts to effect the conversion of alkenes, CO, and methanol to esters, the carbalkoxylation of alkenes, has been known for a number of years.[15-19] The stoichiometric reaction of a metal alkoxide with CO has not been often examined.[20-22] The preparation of the diester platinum complex[20]

$$(PPh_3)_2PtCl_2 + 2KOH + 2CH_3OH + 2CO \rightarrow 2KCl + 2H_2O + (PPh_3)_2Pt(CO_2CH_3)_2$$

and the rapid carbonylation of $BuOCo(CO)_4$[21]

$$BuOCo(CO)_4 \xrightarrow{CO} BuOC(O)Co(CO)_4$$

have been observed although no mechanistic data were reported. The carbonylation of $Pt(dppe)(CH_3)(OCH_3)$ occurs by an associative process with carbonylation of the methoxy functionality occurring in preference to the carbonylation of the methyl.[22]

$$Pt(dppe)(CH_3)(OCH_3) + CO \rightarrow Pt(dppe)(CH_3)(C(O)OCH_3)$$

Table I. Carbonyl Stretching Frequencies (cm^{-1}) of $Ir(CO)_3(PPh_3)_2^+$ as a Function of the Counterion

OPh^- [a]	OPr^- [a]	OMe^- [b]	ClO_4^- [b]	BPh_4^- [c]
2070 (m)	2080 (w)	2075 (w)	2077 (w)	2070 (w)
2028 (s)	2041 (s)	2030 (m)	2020 (s)	2015 (s)
2016 (m)			1997 (s)	1997 (s)

[a] Toluene. [b] KBr. [c] KBr (in THF only 2010 cm^{-1}).

The compound *trans*-$MeOIr(CO)(PPh_3)_2$ is prepared in 95% yield by suspending 0.5 g of *trans*-$ClIr(CO)(PPh_3)_2$ and 0.3 g of CH_3ONa in 40 mL of THF with stirring for 14 h in an inert-atmosphere glovebox after which time the THF is removed and the product extracted into 30 mL of benzene and filtered with a sintered glass suction funnel (fine). The product *trans*-$MeOIr(CO)(PPh_3)_2$ may be recrystallized from benzene/hexane giving a bright yellow microcrystalline solid with $\nu(CO) = 1936$ cm^{-1} in benzene and ^1H NMR (multiplet centered at 7.17 ppm and a singlet at 3.66 ppm, in benzene-d_6) consistent with the formulation. A similar reaction leads to *trans*-*n*-$PrOIr(CO)(PPh_3)_2$ or *trans*-$PhOIr(CO)(PPh_3)_2$. Care must be taken to avoid traces of H_2O that will lead to the hydroxy complex *trans*-$HOIr(CO)(PPh_3)_2$. The reaction with water is described more thoroughly below.

Reaction of 0.2 g of the alkoxyiridium complexes in 20 mL of toluene in a pressure bottle at 20 psi of CO for 48 h results in $ROC(O)Ir(CO)_2(PPh_3)_2$ which can be isolated as pale yellow crystals in good yield by filtering the solution, adding hexane, and storing in a freezer under 1 atm of CO. The infrared and ^1H NMR spectra[23] are in agreement with those previously described for $MeOC(O)Ir(CO)_2(PPh_3)_2$, prepared by nucleophilic attack of CH_3O^- on $[Ir(CO)_3(PPh_3)_2]ClO_4$, and are consistent with the formulation.[24]

Monitoring the reaction of the methoxide complex with CO in toluene by infrared spectroscopy showed very rapid growth of absorptions at 2080, 2041, 1992, and 1945 cm^{-1}. The absorptions at 1992 and 1945 cm^{-1} continued to grow while those at 2080 and 2041 cm^{-1} decreased over a period of 2 h. Treatment of a suspension of *trans*-$MeOIr(CO)(PPh_3)_2$ in 3/1 hexane/toluene with CO at −78 °C allowed isolation of a solid which contains a sharp strong absorption at 2030 cm^{-1} in addition to a weaker peak at 2075 cm^{-1} in KBr. The high-frequency absorptions are best assigned to $Ir(CO)_3(PPh_3)_2^+$.[24-26] Similar reactions with *trans*-*n*-$PrOIr(CO)(PPh_3)_2$ and *trans*-$PhOIr(CO)(PPh_3)_2$ give similar results; however, some $[Ir(CO)_3(PPh_3)_2]^+OPh^-$ persists after 2 days.

The influence of counterion on the infrared spectrum of metal carbonyl anions is well established; the influence of the counteranion on carbonyl stretches of cationic species is not well established. To be certain that the infrared spectra observed correspond to $Ir(CO)_3(PPh_3)_2^+$, we have prepared this cation as the ClO_4^- and BPh_4^- salts. The infrared spectra are compared to those of the intermediates observed in the carbonylation in Table I. The infrared spectra are similar but not identical (it should be noted that the carbonyl stretching bands are very sharp regardless of the counterion). To clarify these observations the carbonylation of *trans*-$PhOIr(CO)(PPh_3)_2$ was accomplished in the presence of an excess (20-fold) of $NaBPh_4$ in THF. The high-frequency absorptions observed in the absence of BPh_4^- were greatly reduced in magnitude and

---

[†] Alfred P. Sloan Research Fellow

(1) Calderazzo, F.; Cotton, F. A. *Inorg. Chem.* **1962**, *1*, 30.

(2) Basolo, F.; Butler, S.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074.

(3) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.

(4) Nicholas, K.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *78*, 133.

(5) Bilder, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889.

(6) Bergman, R. G.; Wax, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 7028.

(7) Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806.

(8) Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1967**, *10*, 101.

(9) Boschetto, D. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1969**, *91*, 4313.

(10) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

(11) McHugh, T. M.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2323.

(12) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4411.

(13) Blake, D. M.; Kubota, M.; Smith, S. A. *Inorg. Chem.* **1971**, *10*, 1430.

(14) Baltusis, L. M.; Casey, C. P. *J. Am. Chem. Soc.* **1982**, *104*, 6347.

(15) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712.

(16) Fenton, D. M.; Steinward, P. J. *J. Org. Chem.* **1972**, *37*, 2034.

(17) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974; p 233.

(18) Fuchikama, T.; Ohishi, K.; Ojima, I. *J. Org. Chem.* **1983**, *48*, 3803.

(19) Alper, H.; Despeyroux, B.; Woell, J. *Tetrahedron Lett.* **1983**, *24*, 5691.

(20) Banditelli, G.; Bonati, F.; Minghetti, G. *Synth Inorg. Met.-Org. Chem.* **1973**, *3*, 415.

(21) Huckaby, J. L.; Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 6150.

(22) Bryndza, H. E., the 11th International Conference on Organometallic Chemistry, Callaway Gardens, Oct 1983.

(23) $MeOC(O)Ir(CO)_2(PPh_3)_2$: IR (KBr) 1982 (s), 1935 (vs), 1636 (m), 1092 (w), 1053 (m) cm^{-1}, (C_6H_6) 1994 (s), 1939 (vs), 1636 (m) cm^{-1}; ^1H NMR (δ) 7.04 (m), 3.17 (s). *n*-$PrOC(O)Ir(CO)_2(PPh_3)_2$: IR (KBr) 1983 (s), 1934 (vs), 1640 (m), 1088 (w), 1037 (m) cm^{-1}, (C_6H_6) 1994 (s), 1937 (vs), 1635 (m) cm^{-1}; ^1H NMR (δ) 7.05 (m), 3.67 (t), 1.4 (m), 0.91 (t). $PhOC(O)Ir(CO)_2(PPh_3)_2$: IR (KBr) 1985 (s), 1938 (vs), 1675 (m) cm^{-1}. In solution an equilibrium between $PhOC(O)Ir(CO)_2(PPh_3)_2$ and $Ir(CO)_3(PPh_3)_2OPh$ complicates the spectra.

(24) Angoletta, M.; Caglio, G.; Malatesta, L. *J. Chem. Soc.* **1965**, 6974.

(25) Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2909.

(26) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1365.

the absorption at 2010 cm^{-1} (characteristic of $Ir(CO)_3(PPh_3)_2{}^+BPh_4{}^-$ in solution) was strong, providing further confirmation of the identity of the intermediate. Conductance data on the reaction mixture from carbonylation of *trans*-$PhOIr(CO)(PPh_3)_2$ also indicate the formation of ionic species.[27]

The formation of the formates from alkoxides at the iridium upon carbonylation is best described as a displacement followed by nucleophilic attack on the cationic carbonyl complex.[28]

$$\textit{trans}\text{-}MeOIr(CO)(PPh_3)_2 + CO \rightarrow [Ir(CO)_2(PPh_3)_2OMe] \xrightarrow{CO} [Ir(CO)_3(PPh_3)_2]^+OMe^- \rightarrow MeOC(O)Ir(CO)_2(PPh_3)_2$$

The nucleophilic attack on a cationic carbonyl has ample literature precedence.[24,29] This mechanism is in contrast to either a MeO$^-$ migration (within the coordination sphere of the iridium) or a CO insertion but is consistent with the observation of $Ir(CO)_3(PPh_3)_2{}^+$ as an intermediate in the carbonylation. The step that leads to the conversion of the alkoxy into a carboalkoxy is the well-documented nucleophilic attack on the carbon of the coordinated carbon monoxide and has been previously demonstrated for MeO$^-$ attack on $Ir(CO)_3(PPh_3)_2{}^+$.[24] It is surprising that the alkoxide could be so readily displaced and that the reaction can proceed cleanly in high yield.

The methoxy complex had previously been reported to be unstable,[30] but in the absence of H_2O it is a quite stable complex. The preparation of the alkoxyiridium complexes require dried solvents and reagents. In the presence of H_2O the hydroxy complex is readily formed.

$$\textit{trans}\text{-}MeOIr(CO)(PPh_3)_2 + H_2O \rightarrow \textit{trans}\text{-}HOIr(CO)(PPh_3)_2 + CH_3OH$$

The hydroxy complex is a light yellow powder with ν(CO) at 1925 cm^{-1} and ν(OH) at 3600 cm^{-1} in KBr. Use of D_2O leads to trans-$DOIr(CO)(PPh_3)_2$ with a ν(OD) of 2658 cm^{-1}. The hydroxy complex does not react with CO under conditions similar to the methoxy analogue, indicating a stronger iridium–oxygen bond for the hydroxy complex.

The displacement, nucleophilic attack mechanism for the carbonylation of *trans*-$ROIr(CO)(PPh_3)_2$ suggests a careful reexamination of carbonylation of metal–oxygen bonds may be necessary. It also offers a new possibility for reaction of alkenes or alkynes with metal–oxygen bonds.

Acknowledgment. We thank Johnson Matthey, Inc., for a generous loan of $IrCl_3 \cdot xH_2O$, the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research, the Alfred P. Sloan Foundation for a fellowship to J.D.A., and the Graduate School, SUNY at Buffalo, for a fellowship to W.M.R.

Registry No. $[Ir(CO)_3(PPh_3)_2]^+OPh^-$, 94070-37-8; $[Ir(CO)_3(PPh_3)_2]^+OPr^-$, 94070-36-7; $[Ir(CO)_3(PPh_3)_2]^+OMe^-$, 94070-35-6; $[Ir(CO)_3(PPh_3)_2]^+ClO_4{}^-$, 15738-08-6; $[Ir(CO)_3(PPh_3)_2]^+BPh^{4-}$, 59809-88-0; *trans*-$MeOIr(CO)(PPh_3)_2$, 94070-38-9; *trans*-*n*-$PrOIr(CO)(PPh_3)_2$, 94070-39-0; *trans*-$PhOIr(CO)(PPh_3)_2$, 94070-40-3; $MeOC(O)Ir(CO)_2(PPh_3)_2$, 15522-78-8; $PrOC(O)Ir(CO)_2(PPh_3)_2$, 63397-73-9; $PhOC(O)Ir(CO)_2(PPh_3)_2$, 94070-41-4; *trans*-$HOIr(CO)(PPh_3)_2$, 32356-70-0; *trans*-$DOIr(CO)(PPh_3)_2$, 94070-42-5; *trans*-$ClIr(CO)(PPh_3)_2$, 59246-46-7.

---

(27) Conductance data were obtained in THF from a platinum black dipping electrode with a Sybron/Barnstead conductivity bridge (Model PM-70 CB) on 5 × 10^{-3} M solutions at 25 °C.

sol	$\overline{L}$, Ω^{-1} cm^{-1}
THF	$<8.86 \times 10^{-8}$ [a]
THF, CO	$<8.86 \times 10^{-8}$ [a]
$PhOIr(CO)(PPh_3)_2$	$<8.86 \times 10^{-8}$ [a]
$PhOIr(CO)(PPh_3)_2$, CO	1.95×10^{-6}
$Ir(CO)_3(PPh_3)_2BPh_4$	9.46×10^{-5}

[a] Below the limits of detection for instrument.

(28) With the current data we cannot rule out two competing mechanisms, only state that some portion proceeds through the cation.

(29) Kruck, T.; Noack, M. *Chem. Ber.* **1964**, *97*, 1693.

(30) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1370.

η^2-Acyl Complexes of Group 4 Metals and of Actinides[†]

Peter Hofmann* and Peter Stauffert
Anorganisch-chemisches Institut der
Technischen Universität München, D-8046 Garching, FRG

Kazuyuki Tatsumi* and Akira Nakamura
Department of Macromolecular Science, Faculty of Science
Osaka University, Toyonaka, Osaka 560, Japan

Roald Hoffmann*
Department of Chemistry, Cornell University
Ithaca, New York 14853

Received November 26, 1984

Summary: The electronic and geometrical structure and reactivity of η^2-acyl complexes of group 4 transition metals and of actinides is the subject of this paper. We find and rationalize the preference for the O-inside η^2-acyl conformer of Ti and Zr bis(cyclopentadienyls) and approximately equal energy O-outside and O-inside conformers for the related U and Th complexes. We also find an unexpected η^1 minimum in the O-outside surfaces. This η^1-acyl can serve as an intermediate in the interconversion of the two η^2 isomers.

The carbonylation chemistry of bis(cyclopentadienyl) dialkyls or diaryls, haloalkyls, and related derivatives of group 4 d metals[1] and of actinides[2,3] shows many interesting facets. The isolable CO insertion products all

---

[†] Dedicated to Prof. Günther Wilke on his 60th birthday.

(1) (a) $Cp_2Ti(COCH_3)Cl$ was formed by the reaction between $Cp_2Ti(CO)_2$ and CH_3COCl, Fachinetti, G; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (b) Fachinetti, G.; Floriani, C.; Stöckli-Evans, H. *Ibid.* **1977**, 2297–2302. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109 and references therein. (d) Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 121–127 and references therein. (e) Jeffery, J.; Lappert, M. F.; Luong-Thi, M. T.; Webb, M. *J. Chem. Soc., Dalton Trans.* **1981**, 1593–1605. (f) Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1289–1297. (g) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *222*, 79–88. (h) Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305–317; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311.

(2) (a) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *No. 131*, 1–29. (b) Fagan, P. J.; Maatta, E. A.; Marks, T. J. *Ibid.* **1981**, *152*, 52–78. (c) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396. (d) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *Ibid.* **1981**, *103*, 2206–2220. (e) Marks, T., private communication.

(3) (a) For a CO insertion into the U═C double bond in $Cp_3UCHP(CH_3)(C_6H_5)_2$, see: Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869–871. (b) Remarkably facile CO insertion into M–C and M–N bonds has also been found for Cp_3ThR, Cp_3UR, and Cp_3UNR_2: Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484–3491. Paolucci, G.; Rossetto, G.; Zanella, P.; Yünlü, K.; Fischer, R. D., submitted for publication. For isocyanide insertions into U–C bonds see: Dormond, A.; Elbouadili, A. A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1984**, 749–751. For isocyanide insertions into Zr–R bonds (R = H, CH_3) of $Cp_2{}^*ZrR_2$: Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450–6452.

0276-7333/85/2304-0404$01.50/0