

all the acylsilane, a new set of signals in addition to those of the silene 4 was observed which grew at the expense of the silene concentration such that by the end of a further 24 h photolysis all the silene had disappeared. (This reaction of the silene did not occur in the dark over several days.) The new compound was identified as the substituted dihydrobenzocyclobutene 5 based on its Si-H infrared absorption, the presence of only two Me-aryl groups, and the existence of a 2-proton AB system.⁷ Formation of the dihydrobenzocyclobutene implies a photochemical insertion into a relatively unactivated C-H bond, possibly by a radical process although this is not yet proven.⁸ This reaction is not an isolated example since the related (2,6-diethylbenzoyl)polysilane on photolysis gives a related dihydrobenzocyclobutene.⁹

When the mesitylsilane 3 was photolyzed in solution with hexamethylsilane 6, in addition to the formation of 4 and 5 as expected, weak signals for a new compound, 7, were observed. On standing overnight in the dark, the concentration of the silene 4 significantly diminished and considerable 7 and tetramethylethylene were formed, as well as weak signals due to a further compound, 8. The spectroscopic properties of 7, in particular a highly shielded silicon signal at -118 ppm as well as a less shielded silicon at -36 ppm which bore two methyl groups, are in accord with its being the disilacyclopropane 7,¹⁰ formed as a result of the silene reacting with the silirane in the dark and acquiring the elements of dimethylsilylene, although whether "free" dimethylsilylene is the actual reactant is not yet established. It is obvious that compound 7 is highly hindered sterically, since each methyl of the mesityl group has a separate NMR absorption.

The identity of the second new compound 8 then became a matter of some interest since on standing in the dark at room temperature over several hours 7 was cleanly converted to 8 (80% conversion in 24 h and virtually quantitative conversion in 2 days). Furthermore 8 could be rapidly reconverted to 7 by brief (20-60 min) photolysis at $\lambda > 360$ nm, and cycling back and forth between 7 and 8 could be carried out repeatedly without side reactions.¹¹ The structure assigned to 8¹² (or its isomer in which the

groups attached to the two ring silicon atoms are interchanged) is supported by spectroscopic data and in particular the fact that the proton chemical shift of one of the three methyl groups attached to carbon moved upfield as a consequence of its attached carbon changing from sp^2 to sp^3 hybridization. The aromatic protons of 7 at 6.75 ppm moved upfield to 5.55 and 5.61 ppm as a result of the change to vinyl-type protons. In addition the absorption at -118 ppm of the highly shielded ring silicon bearing two trimethylsilyl groups moved downfield to -52 ppm as a result of the relief of steric strain: comparable shifts have been observed before as in silacyclopropanes (-49.3 ppm¹³) and silacyclobutanes (18.5 ppm¹⁴).

The clean, facile, reversible 1,3-isomerizations involved in the interconversions of 7 and 8 under very mild conditions, temperatures of about 25 °C and wavelengths above 360 nm, appear to constitute an exceptional situation in which ring strain energy closely balances loss of aromatic stabilization energy. We are continuing to explore this and related systems.

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(12) Properties of 8: ¹H NMR δ 0.22, 0.23, 0.30 (each 9 H, s, Me₃Si), 0.45, 0.59 (each 3 H, s, Me₃Si), 1.40, 1.73, 2.36 (each 3 H, MeC), 5.55, 5.61 (2 H, br, HC- sp^2); ¹³C NMR δ 1.08, 1.43, 1.96 (each Me₃Si), -0.68, 1.36 (Me₃Si), 20.95, 25.67, 33.19 (each MeC) 35.39 (sp^3 -C Me), 125.19, 127.49, 131.18, 133.39, 146.06, 158.09 (C- sp^2); ²⁹Si NMR δ -52.3 (Si(SiMe₃)₂), -16.1, -14.4, -11.4 (two Me₃Si plus SiMe₂), 14.0 (Me₃SiO); MS calcd 452.2239, found 452.2240. Anal. Calcd for C₂₁H₂₄Si₅O-C₆H₃: C, 60.36; H, 10.51. Found: C, 60.87; H, 10.58.

(13) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2273.

(14) Seyferth, D.; Duncan, D. P.; Schmidbaur, H.; Holl, P. *J. Organomet. Chem.* **1978**, *159*, 137.

(5) Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Organometallics* **1982**, *1*, 994.

(6) Properties of 4: ¹H NMR δ -0.16 (18 H, s, two Me₃Si, accidental overlap), 0.29 (9 H, s, Me₃Si(O?)), 2.35 (9 H, s, o, + p-Me, accidental overlap), 6.70 (2 H, br s, aromatic); ¹³C NMR δ 0.89, 1.34, 2.05 (Me₃Si), 21.25 (Me-Ar, accidental overlap), 141.75, 136.25, 128.52, 136.83 (C_{ipso}, o, m, p of mesityl), 197.66 (C=Si); ²⁹Si NMR δ -12.94, -11.92 (Me₃Si), 14.06 (Me₃SiO), 37.75 (Si=C).

(7) Properties of 5: IR (neat) 2067 cm⁻¹ (SiH); ¹H NMR δ -0.04, 0.07, 0.34 (each 9 H, s, Me₃Si), 2.13, 2.30 (each 3 H, s, Me), 3.28, 3.41 (2 H, AB system, J_{AB} = 14.5 Hz), 3.99 (1 H, s, SiH), 6.67 (2 H, br, aromatic); ¹³C NMR (DEPT) δ 0.14, 1.05, 2.22 (each Me₃Si), 17.08, 22.14 (MeAr), 46.00 (CH₂), 75.55 (COSiMe₃), 121.74, 129.76 (each CH aromatic), 132.65, 138.68, 139.49, 148.61 (each C aromatic); ²⁹Si NMR δ -14.33, -16.45 (Me₃Si), 12.93 (Me₃SiO), -55.62 (SiH) (J_{Si-H} = 164 Hz) ppm; MS, m/e 394 (M⁺). Anal. Calcd for C₁₉H₃₈Si₄O: C, 57.80; H, 9.70. Found: C, 57.44; H, 9.71.

(8) A related insertion of a disilene into a mesityl CH₃ group has been described: Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070.

(9) These results will be described in the full paper.

(10) Properties of 7: ¹H NMR δ -0.07, -0.02 (each 9 H, s, Me₃Si), 0.44 (Me₃Si(O?)), 0.44, 0.63 (each 3 H, s, Me₂Si), 2.11, 2.42, 2.83 (each 3 H, s, MeAr), 6.75 (2 H, br s, aromatic); ¹³C NMR δ 1.87, 1.87, 2.63 (Me₃Si), -4.07, 0.63 (Me₂Si), 20.97, 22.43, 22.51 (MeAr), 62.02 (COSiMe₃), 129.50, 129.85, 136.36, 136.68, 137.73, 142.66 (aromatic); ²⁹Si NMR δ -118.5 (Si(Me₃Si)₂), -35.6 (SiMe₂), -11.5, -8.2 (each Me₃Si), 12.01 (Me₃SiO); MS calcd 452.2239, found 452.2245.

(11) During these interconversions the 5 present remains unchanged and hence is not involved in the interconversion of 7 and 8.

Homogeneous Catalytic Activation of Vinyl C-H Bonds. Stereoselective H-D Exchange in Neohexene

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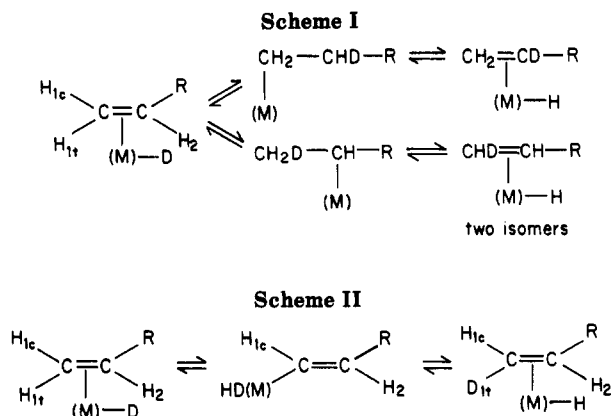
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Summary: Deuterium-hydrogen exchange between benzene-*d*₆ and neohexene (3,3-dimethylbutene) is catalyzed by [(*i*-Pr₃P)₂IrH₅] at room temperature. The rate of exchange of the terminal vinyl proton trans to the *tert*-butyl group is >10 times that of the proton geminal to the *tert*-butyl group. This shows that, for certain olefins at least, activation of the vinyl C-H bond can occur more readily than addition-elimination reactions of metal hydride across the double bond.

There are numerous examples of H-D exchange reactions in arenes and alkanes, many of which are catalyzed

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by homogeneous transition-metal systems.^{1,2} Similar exchanges of vinylic hydrogens with deuterated solvents have also been observed.^{1,3} In these homogeneous systems, there appears to be a consensus that the mechanism for H-D exchange in arenes and olefins proceeds via prior formation of a π -complex. For olefins, isotopic exchange^{2,3} and isomerization⁴ are generally attributed to either (a) reversible allylic hydrogen transfer to the metal and π -allyl formation or (b) addition of a metal hydride to the olefin to yield a metal alkyl followed by β -hydride elimination. With arenes, on the other hand, the step after coordination is most often considered to be insertion of the metal into an Ar-H bond, i.e., reversible metal-aryl formation. The analogous path with olefins, which would involve a metal-vinyl complex, appears to have been generally disregarded. We report here that $\text{Ir}(\text{i-Pr}_3\text{P})_2\text{H}_5$ is an efficient catalyst for the selective activation of the *trans* vinyl C-H bond in neohexene (3,3-dimethylbutene). This is remarkable because it demonstrates that vinylic C-H bond activation can occur more readily than addition-elimination reactions of metal hydrides across the double bond.

We find that deuterium from benzene- d_6 can be rapidly and selectively exchanged with $\text{H}_{1\text{t}}$ of neohexene in the presence of the iridium complex. Exchange between arene C-D and metal-H bonds² provides a source of Ir-D in our experiment. The most noteworthy feature of the transfer of D into the neohexene is its selectivity; deuterium is introduced into a specific terminal position, $\text{H}_{1\text{t}}$, as opposed to substitution at carbon-2, H_2 . This is of course entirely contrary to the anticipated results for the commonly accepted hydrogenation and isomerization mechanisms:^{3,4} since π -allyl formation cannot occur with neohexene, isotopic exchange would have been expected to proceed via addition of metal deuteride to the olefin and β -hydride elimination (Scheme I). The deuterium exchange experiment described here suggests that an alternate path is required, viz., η^1 -vinyl formation followed by reductive elimination (Scheme II), analogous to the generally ac-

cepted mechanism for arene H/D exchange.²

In following the progress of the reaction by ^1H NMR, one observes that in the initial phases of the exchange process,⁵ a $\text{C}_6\text{D}_5\text{H}$ resonance grows as the hydrides on the iridium and hydrogen in the ligands⁶ are exchanged. Some neohexene is also hydrogenated to neohexane, thus presumably producing the coordinatively unsaturated active species.⁷ Over a period of 20 min at 35 °C, one observes that the H_2 resonance of the neohexene (dd, $J_{\text{trans}} = 16.8$, $J_{\text{cis}} = 9.7$ Hz) is replaced by the characteristic resonance of *trans*-CHD=CH-*t*-Bu (dt, $J_{\text{trans}} = 16.8$, $J_{\text{cis}} = 1.6$ Hz).⁸ Since the addition-elimination path would place deuterium either equally in both terminal positions or, more probably, at H_2 ,⁹ one is forced to invoke a different pathway, i.e., metal-vinyl formation. Over several hours, one observes the formation of $\text{CD}_2=\text{CH-t-Bu}$, as a consequence of the addition-elimination process,⁹ but it is clear that reversible metal-vinyl formation (Scheme II) occurs more than 10 times more rapidly than hydride addition-elimination across the olefin (Scheme I).

In view of this result, one might be surprised by the limited number of previous observations of vinylic C-H activation. It should be noted that neohexene is a rather special olefin in that it has no allylic C-H bonds. Most previous isotopic exchange investigations of hydrogenation catalysts directed toward the study of catalyzed isomerization would not generally have attributed the observations to vinylic activation owing to the consequences of allylic C-H activation.¹⁰ In this context, our results suggest that vinyl activation may be much more common and generally important than previously recognized. Furthermore, they suggest that the formation of vinyl-metal intermediates may need to be considered more seriously in some hy-

(5) Concentrations of 0.07 M iridium complex in a solution of ~3:1 mole ratio of C_6D_6 :neohexene produce transfer of approximately 200 H/Ir-h to the benzene at room temperature after an induction period of ~10 min. At these relative concentrations, metalation of the isopropyl ligand takes place and H transfer to the benzene occurs at a rate comparable to transfer from neohexene. At low concentrations of catalyst and neohexene in C_6D_6 , the initial production of $\text{C}_6\text{D}_5\text{H}$ arises from hydride predominantly derived from ligand metalation. At 35 °C deuteration of the *trans* terminal proton is essentially complete within 20 min. No significant quantity of *cis*-CHD=CH-*t*-Bu is observed. After a period of an hour at room temperature the intensity ratio of the terminal vinyl protons to those on the 2-carbon is 1.1 ± 0.05 .

(6) Isotopic exchange with solvent and with ligands has been observed previously: (a) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* 1969, 1963-1972. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1982, 104, 4240-2. (c) Morris, R. H.; Shiralian, M. J. *Organomet. Chem.* 1984, 260, C47-C51. (d) Chaudret, B. *J. Organomet. Chem.* 1984, C33-7.

(7) Although we believe the principal active species is derived from either a tri- or monohydride formed by removal of two or four hydrogens from the pentahydride by formation of neohexane from neohexene, we cannot exclude the intermediacy of a polynuclear catalyst.

(8) This preparation of *trans*-CHD=CH-*t*-Bu may be useful synthetically in the preparation of MCHDCHD-t-Bu complexes for stereochemical studies [(a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demurs, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* 1974, 96, 2814. (b) Labinger, J. A.; Hart, D. W.; Seiber, W. E.; Schwartz, J. J. *Am. Chem. Soc.* 1975, 97, 3851-3852. (c) Carr, D. B.; Schwartz, J. J. *Am. Chem. Soc.* 1979, 101, 3521-3531.].

(9) In Scheme 1, addition is expected to yield the more stable intermediate with a primary metal-alkyl bond. Elimination from this would yield some material with deuterium at C-2, which is not observed to a significant extent early in the reaction. This mechanism does, however, provide a route for equilibrating the terminal vinyl positions. In the event, significant amounts of *cis*-CHD=CH-*t*-Bu or *cis*-CHD=CD-*t*-Bu are not observed owing to the faster metal-vinyl formation which rapidly converts them into $\text{DC}_2=\text{CH-t-Bu}$ and $\text{CD}_2=\text{CD-t-Bu}$. Addition-elimination in the opposite sense, via an intermediate with a secondary metal-alkyl bond, would provide a path for isomerization in olefins with allylic hydrogens. Such an intermediate, with a monodeuteriomethyl group, would not lead to the observed selectivity in the case of neohexene.

(10) The interactions with olefins containing α -hydrogens often leads to *n*-allyl and *n*-diene complexes or catalytic disproportionation of the olefin to diene and alkane. See, e.g.: Clerici, M. G.; DiGiacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* 1975, 84, 379-388.

(1) (a) Shilov, A. E. "Activation of Saturated Hydrocarbons by Transition Metal Complexes"; D. Reidel Publishing Co.: Dordrecht, 1984 and references therein. (b) Garnett, J. L. *Catal. Rev.* 1971, 229-268. (c) Webster, D. E. *Adv. Organomet. Chem.* 1977, 15, 147.

(2) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* 1965, 843-855. (b) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* 1970, 92, 5234-5. (c) Ittel, S. D.; Tolman, C. A.; English, A. P.; Jesson, J. P. *J. Am. Chem. Soc.* 1976, 98, 6073-5. (d) Parshall, G. W. *Catalysis* 1977, 334. (e) Jones, W. D. *J. Am. Chem. Soc.* 1984, 106, 1650-1663; 1985, 107, 620-631 and references therein.

(3) Cramer, R. *J. Am. Chem. Soc.* 1966, 88, 2272; *Acc. Chem. Res.* 1968, 1, 186-191.

(4) (a) Tolman, C. A.; Faller, J. W. In "Catalysis by Transition Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 13-109. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (c) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.

drogenation, isomerization, and olefin dimerization mechanisms.¹¹⁻¹⁴

Registry No. C₆D₆, 1076-43-3; (*i*-Pr₃P)₂IrH₅, 53470-70-5; neohexene, 558-37-2.

(11) Although metallacycles have been proposed, the interactions of ethylene with (C₅H₅)₂Ti₂ may involve vinyl activation (Pez, G. P. *J. Chem. Soc., Chem. Commun.* 1977, 560-561. McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1976, 98, 6529-36.). Although conventional olefin dimerization paths may well be operative, vinyl activation might be considered in some propene dimerizations [Baudry, D.; Cormier, J.-M.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* 1984, 277, 99-103. Green, M. L. H.; Knight, J. *J. Chem. Soc., Dalton Trans.* 1974, 311-319.

(12) Stoichiometric vinyl activation has been observed with some clusters: (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organomet. Chem.* 1974, 80, C53. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* 1975, 85, C29. (c) Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Mann, A. L.; Raithby, P. R. *J. Organomet. Chem.* 1976, 113, C42; *J. Chem. Soc., Chem. Commun.* 1980, 547.

(13) Metal-vinyl complexes have also been obtained with some bimetallic systems: Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Tayler, G. E. *J. Organomet. Chem.* 1980, 198, C43. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* 1982, 104, 4955; 1984, 106, 644-652; 1984, 106, 3474-3484 (this system also shows modest oligomerization catalysis). (c) Franzeb, K.-H.; Kreiter, C. G. *J. Organomet. Chem.* 1983, 246, 189. (d) King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* 1983, 105, 4846-8.

(14) Olefins containing donor atoms also undergo vinyl activation: (a) Kliegman, J. M.; Cope, A. C. *J. Organomet. Chem.* 1969, 16, 309. (b) Van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* 1975, 85, 249. (c) Foot, R. J.; Heaton, B. J. *J. Chem. Soc., Chem. Commun.* 1973, 838. (d) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* 1976, 98, 3874-3884. (e) Aumann, R.; Henkel, F.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 204.

Preparation of Reactive Low-Valent Bis(diphenylphosphino)methane-Bridged Mo-Ru Complexes. Facile Heterobimetallic Activation of Molecular Hydrogen

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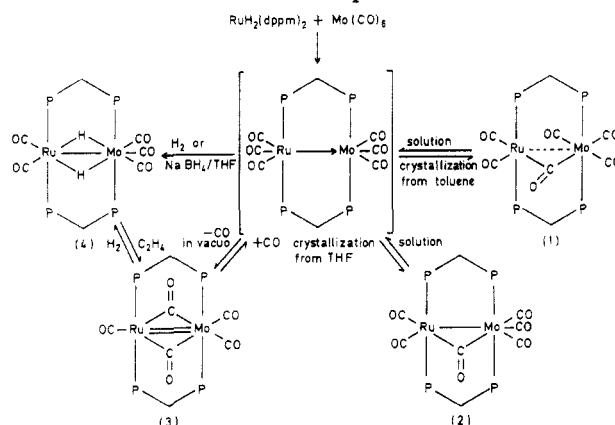
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Summary: The reaction between RuH₂(dppm)₂ (dppm = bis(diphenylphosphino)methane) and Mo(CO)₆ at 80 °C produces MoRu(CO)₆(dppm)₂ which exists in three different interconvertible forms whether in solution, recrystallized from toluene (1) or tetrahydrofuran (2). MoRu(CO)₆(dppm)₂ loses CO reversibly at 80 °C in toluene in vacuo to give MoRu(CO)₅(dppm)₂ (3) which contains two bridging carbonyl groups. Dihydrogen adds to 3 at room temperature to give the dihydrido-bridged complex MoRuH₂(CO)₅(dppm)₂ (4). The crystal structure of 1 (MoRu(CO)₆(dppm)₂·5C₆H₅CH₃) shows the complex to contain a long Mo-Ru distance and an "atypical" semibridging carbonyl group with a long C-O bond, in agreement with its low stretching frequency.

Heterobimetallic complexes are attracting considerable attention but as noted earlier, relatively few unsaturated complexes have been prepared and their reactivity studied.^{1,2} These compounds are of particular interest when

Scheme I. Preparation and Reactivity of MoRu(CO)₆(dppm)₂: Proposed Structure for the Complexes



they are capable of easy reversible reactions with molecules like CO or H₂. Thus the production of heterobimetallic dihydrides, with each hydride possessing a distinct character, would be a key step in the reduction of polar molecules like CO.³ Following our interest in heterobimetallic complexes,^{4,5} we attempted the preparation of such molybdenum-ruthenium compounds. These compounds have not received much attention,^{6,7} whereas Rh-Mo complexes, for example, are known.^{3,8} We used RuH₂(dppm)₂⁹ as starting material, as dppm seems a very good ligand for stabilizing heterobimetallic complexes.¹⁰ We describe the preparation of MoRu(μ-CO)(CO)₅(dppm)₂, a reactive complex which readily loses 1 mol of CO to give an unsaturated complex. Its reactivity in particular toward H₂ is of special interest.

RuH₂(dppm)₂ reacts with 1 equiv of Mo(CO)₆ in toluene at 80 °C to give an orange solution from which orange crystals analyzing for MoRu(CO)₆(dppm)₂ (1) deposit after being cooled. Recrystallization from THF affords another compound (2) of the same formula as yellow crystals. Both compounds are shown by EDAX¹¹ to contain molybdenum and ruthenium. 1 and 2 have different infrared spectra in the 2100-1600 cm⁻¹ region in the solid state. One striking difference is the presence of a band at 1685 cm⁻¹ for 1 which shifts to 1715 cm⁻¹ in the case of 2. Nevertheless, both compounds when dissolved in CH₂Cl₂ or THF exhibit the same infrared spectrum which is different from the solid-state spectra. In that case no band below 1800 cm⁻¹ is observed.¹² As expected the NMR spectra of 1 and

(2) Breen, M. J.; Duttera, M. R.; Geoffroy, G. L.; Novotnak, G. C.; Roberts, D. A.; Shulman, M. P.; Steinmetz, G. R. *Organometallics* 1982, 1, 1009.

(3) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* 1983, 105, 7574.

(4) Sabo, S.; Chaudret, B.; Gervais, D. *J. Organomet. Chem.* 1983, 258, C19.

(5) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Nouv. J. Chim.* 1983, 7, 679. Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *Organometallics* 1985, 4, 935.

(6) Vollhart, K. P. C.; Weidman, T. W. *Organometallics* 1984, 3, 82.

(7) Sabo, S.; Chaudret, B.; Gervais, D. *J. Organomet. Chem.*, in press.

(8) (a) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* 1982, 1001; (b) *J. Chem. Soc., Dalton Trans.* 1984, 1693.

(9) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* 1984, 1635.

(10) See, for example: Blagg, A.; Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* 1984, 1815 and references therein.

(11) EDAX: energy dispersive analysis by X-ray.

(1) (a) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Chapter 40; (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. G. *J. Am. Chem. Soc.* 1983, 105, 1069.