signed to the equatorial carbonyls **g** and **i**. These assignments are based upon earlier observations that the resonances of axial carbonyls in this type of cluster occur at lower field than those of equatorial carbonyls.[2,19]

$(\mu\text{-H})(\eta^5\text{-}C_5H_5)MoOs_3(CO)_{14}$. Compound III was characterized by its FT-ICR mass spectrum and its ^1H NMR spectrum. The mass spectrum showed a parent ion peak which corresponds to the molecular formula $^1H_6{}^{12}C_{19}{}^{16}O_{14}{}^{98}Mo^{192}Os_3$ (m/e(obsd) 1131.97; m/e(calcd) 1131.88). The loss of each of the first 13 carbonyls was visible in a single spectrum, and the Mo_2Os_3 stoichiometry was established from the relative intensities within each multiplet. The ^1H NMR spectrum in $CDCl_3$ at 28 °C consists of a singlet of relative intensity 5 at 5.28 ppm which is assigned to the cyclopentadienyl group and a singlet of relative intensity 1 at −20.51 ppm which is assigned to a bridge hydrogen. A proposed structure which satisfies the 18-electron rule is shown in Figure 7. The crystal structure of an isoelectronic analogue $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$[26] has been reported. Several other mixed-metal clusters, i.e., $HReOs_3(CO)_{16}$,[20,21] $H_2MnOs_3(CO)_{15}{}^{1-}$, and $H_2FeOs_3(CO)_{14}{}^{1-}$[22] have also been suggested to have the same type of structure.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE 84-11630. We thank Tao-Chin Lin Wang, Annjia T. Hsu, and Professor Alan G. Marshall for FT/ICR mass spectra and C. R. Weisenberger for high-resolution mass spectra. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019).

Registry No. I, 101032-01-3; I·C_6H_6, 101054-44-8; II, 101032-02-4; III, 101032-03-5; $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7; $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$, 56200-27-2.

Supplementary Material Available: Listing of anisotropic thermal parameters and structure factor amplitudes (73 pages). Ordering information is given on any masthead page.

---

[26] Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* 1981, *20*, 4124.

Communications

Trapping of a Reactive Tetraruthenium Imido Cluster with Diphenylacetylene

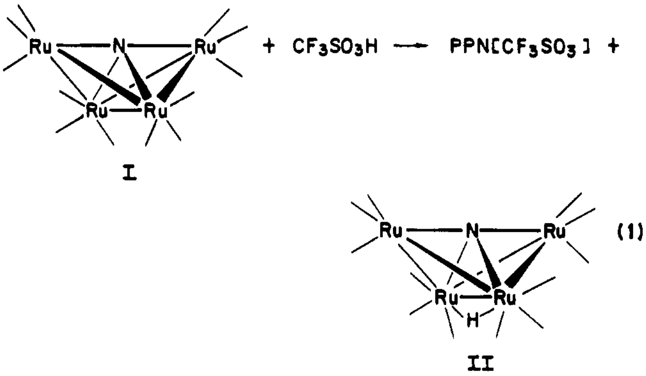
Margaret L. Blohm[1] **and Wayne L. Gladfelter***[2]

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received December 10, 1985

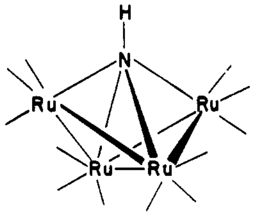
Summary: Diphenylacetylene traps the intermediate imido cluster formed during the protonation of $[Ru_4N(CO)_{12}]^-$. Structural characterization of the new cluster $Ru_4(NH)(PhCCPh)(CO)_{11}$ revealed the first example of a tetrabridging imido ligand.

The reactivity of main-group atoms exposed along the edges or faces of metal clusters is receiving a great deal of attention. In particular it has been shown that the carbon atom in carbido clusters can be protonated,[3,4] alkylated,[5] and acylated[6] and also that CO can migrate from an adjacent metal onto the carbon to form a ketenylidene (CCO) ligand.[7] Fewer studies have reported chemistry of the nitrogen atom in nitrido clusters.[8] Recently, we reported spectroscopic evidence that the following protonation (eq 1) occurs via the intermediate imido cluster III.[9] Unfortunately, III could not be isolated as a crystalline solid. We have discovered, however, that diphenylacetylene is an effective reagent for trapping the spectroscopically observed intermediate in this protonation and that the product does indeed contain the first example of a stable μ_4–NH ligand.



I

II



III

Addition of 1 equiv of CF_3SO_3H to a CH_2Cl_2 solution of $PPN[Ru_4N(CO)_{12}]$,[10] forms a bright purple solution. Immediate addition of excess diphenylacetylene (eq 2) to the purple intermediate results in the isolation of two

---

[1] NSF Predoctoral Fellow, 1982–1985.

[2] Alfred P. Sloan Fellow, 1983–1985.

[3] Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* 1979, *101*, 7417.

[4] Hriljac, J. A.; Swepston, P. N.; Shriver, D. F. *Organometallics* 1985, *4*, 158.

[5] Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* 1982, *104*, 5621.

[6] Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimmie, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* 1981, *78*, 668.

[7] Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* 1983, *105*, 7307.

[8] Gladfelter, W. L. *Adv. Organomet. Chem.* 1985, *24*, 41.

[9] Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.*, in press.

[10] Blohm, M. L.; Gladfelter, W. L. *Organometallics* 1985, *4*, 45.

$$\underset{\text{I}}{\mathrm{PPN[Ru_4N(CO)_{12}]}} \xrightarrow[\text{1. } \mathrm{CF_3SO_3H} \quad \text{2. } \mathrm{4PhC{\equiv}CPh,\ 1\ h}]{\mathrm{CH_2Cl_2}} \underset{\text{V}}{\mathrm{Ru_4(NH)(CO)_{11}(Ph_2C_2)}} + \underset{\text{IV}}{\mathrm{Ru_3(NH)(CO)_{10}}} + \mathrm{PPN[Ru_5N(CO)_{14}]} \quad (2)$$

neutral products. Chromatography separated $Ru_3(NH)(CO)_{10}$[9] (10% yield) from bright yellow crystals that analyzed for $Ru_4(NH)(Ph_2C_2)(CO)_{11}$ (V) (41% yield).[11]

A single-crystal X-ray crystallographic analysis of V[12] revealed the tetrahedrally distorted square geometry of ruthenium atoms shown in Figure 1, capped on one side by an unprecedented μ_4-N-H and on the other side by a μ_4-η^2-acetylene. The four ruthenium atoms define a "flattened butterfly" structure where the dihedral angle between the Ru(1)-Ru(2)-Ru(3) and Ru(2)-Ru(3)-Ru(4) planes is 157.9° compared to 103.4° in I. Ignoring the rotational conformation of the phenyl rings, the overall structure conforms to the C_s point group. Further comparison to the structure of I shows that only the hinge M-M bond has been severed. Two of the four Ru-Ru bonds are bridged by carbonyl ligands and are 0.06 Å shorter than the unbridged Ru-Ru bonds. The remaining carbonyls are terminally bound: two to each metal except for Ru(4) which has three. One of the carbonyl ligands, C(4C)-O(4C), on Ru(4) exhibits a slight bending of 171.2 (3)° and a Ru(2)-C(4C) distance of 2.836 (3) Å suggestive of a weak semibridging interaction. The imido nitrogen is bound to all four metals with bond distances ranging from 2.120 (2) (Ru(4)-N) to 2.159 (2) Å (Ru(2)-N). Including the hydrogen atom, which was located (N-H(N) = 0.82 (3)Å), the five-coordinate nitrogen atom exists in a distorted square-pyramidal geometry. All previous structural studies of the NH ligands in clusters report it as a triply bridging ligand.[13-16] Even among organoimido-containing clusters, which is a larger class of compounds,[17-24] only one μ_4-NR has been reported.[24] It was found bridging the square plane of irons in $Fe_4(NEt)(EtNO)(CO)_{11}$. The tetrabridging geometry found here for nitrogen is much more common in phosphorus chemistry; several structurally characterized μ_4-PR groups having been reported.[25-30]

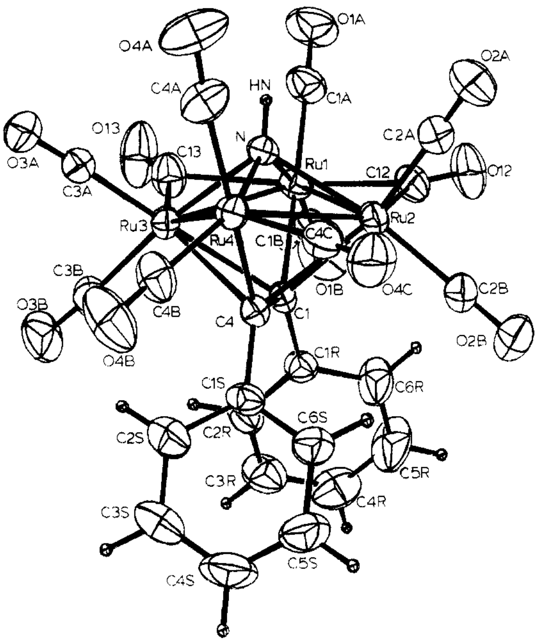
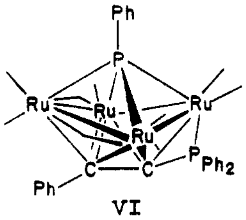
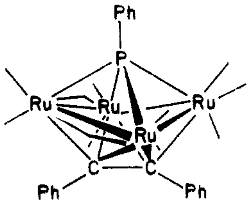


Figure 1. View of $Ru_4(NH)(PhCCPh)(CO)_{11}$ showing the atom labels. The thermal ellipsoids are drawn at the 50% probability level for all atoms except the hydrogens. Selected bond distances (Å): Ru1-Ru2, 2.695 (1); Ru1-Ru3, 2.677 (1); Ru2-Ru4, 2.756 (1); Ru3-Ru4, 2.732 (1); Ru1-N, 2.152 (2); Ru2-N, 2.159 (2); Ru3-N, 2.149 (2); Ru4-N, 2.120 (2); Ru1-C1, 2.220 (2); Ru2-C1, 2.334 (2); Ru3-C1, 2.357 (2); Ru2-C4, 2.473 (2); Ru3-C4, 2.354 (2); Ru4-C4, 2.137 (2); C1-C4, 1.416 (3); N-HN, 0.82 (3). Selected angles (deg): Ru1-Ru3-Ru4, 94.61 (1); Ru1-N-Ru3, 76.99 (7); Ru1-N-Ru4, 137.1 (1); Ru3-N-Ru4, 79.59 (7); Ru1-C1-C4, 127.5 (2); Ru4-C4-C1, 124.2 (2); C1-Ru3-C4, 34.98 (8); C1R-C1-C4, 119.1 (2).

The acetylene group is coordinated to the four metals in a μ_4-η^2-bonding mode. It is very similar to the geometry observed for the acetylene group in the isoelectronic clusters $Ru_4(PPh)(Ph_2PC{\equiv}CPh)(CO)_{10}$ (VI)[30] and $Ru_4(PPh)(PhCCPh)(CO)_{11}$ (VII).[31] Each of these clusters



VI



VII

contains 64 electrons, which as discussed by Lauher and Carty, should give a nearly planar arrangement of metals.[32,33] This differs from the more common μ_4-η^2-bonding mode for acetylenes found in 62-electron butterfly clus-

---

(11) Anal. Calcd for $C_{25}H_{11}NO_{11}Ru_4$: C, 33.16; H, 1.22; N, 1.55. Found, C, 32.80; H, 1.26; N, 1.51. IR ν_{CO} (hexane) 2088 w, 2060 s, 2051 vw, 2034 vs, 2025 m, 2011 m, 1984 m, 1899 vw, 1855 w cm^{-1}; ν_{N-H} (CH_2Cl_2) 3333 vw cm^{-1}. ^{1}H NMR (ppm, $CDCl_3$): 1.97 (t, $J_{^1H-^{14}N}$ = 54 Hz), 6.62 (m).

(12) X-ray diffraction data for $Ru_4(NH)(CO)_{11}[(C_6H_5)_2C_2]$: crystal dimensions, 0.45 × 0.30 × 0.08 mm; crystal system, triclinic; space group, $P\bar{1}$; a = 9.389 (4) Å, b = 9.154 (11) Å, c = 17.485 (3) Å; α = 85.43 (7)°, β = 79.44 (2)°, γ = 70.81 (7)°; Z = 2; absorption coefficient 10.719 cm^{-1}; diffractometer Enraf-Nonius CAD4; radiation graphite-monochromatized Mo Kα; scan range 0-56°; reflections collected 6704 unique, 2304 with $F_o > 2.0\sigma(F_o)$; ρ(calcd) = 2.156 g/cm^3; R = 0.030, R_w = 0.041; molecular formula $C_{25}H_{11}NO_{11}Ru_4$; molecular weight = 905.7 g/mol.

(13) Fjare, D. E.; Keyes. D. G.; Gladfelter, W. L. *J. Organomet. Chem.* **1983**, *250*, 383.

(14) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

(15) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 797.

(16) Bedard, R. L.; Rae, A. D.; Dahl, L. F., personal communication.

(17) Dawoodi, Z.; Mays, M. J.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 433.

(18) Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, C41.

(19) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1982**, *224*, C40.

(20) Barnett, B. L.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 910.

(21) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339.

(22) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765.

(23) Gall, R. S.; Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 4017.

(24) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 387.

(25) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.

(26) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1982**, *224*, C49.

(27) Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, *209*, 85.

(28) Ryan, R. C.; Pittman, C. U.; O'Connor, J. P.; Dahl, L. F. *J. Organomet. Chem.* **1980**, *193*, 247.

(29) Vahrenkamp, H.; Wolters, D. *Organometallics* **1982**, *1*, 874.

(30) Daran, J. C.; Jeannin, Y.; Kristiansson, O. *Organometallics* **1985**, *4*, 1882.

(31) Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066.

(32) Lauher, J. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

(33) Carty, A. J.; MacLaughlin, S. A.; Van Wagner, J.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013.

ters[34-38] by the absence of the fifth M-M bond.

An alternative way of describing the cluster geometry is as a pentagonal bipyramid with two RuL_n fragments, two CR groups, and one NR group in the equatorial plane and two rutheniums in the axial positions. Such a description is consistent with the skeletal electron pair bonding rules which predict a closo seven-vertex cluster when eight skeletal electron pairs are present.[39]

Regarding the trapping reaction itself, the conversion, which occurs under very mild conditions, results in loss of one CO from III. From other studies[9] III (formed in situ as in this study) was found to react with CO to form $Ru_3(NH)(CO)_{10}$ and $PPN[Ru_5N(CO)_{14}]$. Consistent with this, the other two observed products in reaction 2 are $Ru_3(NH)(CO)_{10}$ and $PPN[Ru_5N(CO)_{14}]$; each in small amounts. Conceptually, the addition of the acetylene to III is easy to describe as an insertion of the C≡C into the hinge M—M bond of the cluster. Concomitant unfolding of the wings of the butterfly allow the acetylene to be stabilized by direct interaction with all four metals.

In conclusion, the trapping of $Ru_4(NH)(CO)_{12}$ (III) with diphenylacetylene has allowed the structural characterization of a stable product. Consistent with the mild reaction conditions, the structure of $Ru_4(NH)(PhCCPh)(CO)_{11}$ can be traced back to the structure proposed for III through a small number of steps. This new cluster contains an imido ligand in the novel tetrabridging bonding geometry. The NH group has been implicated as a surface-bound intermediate in the Haber process and in the decomposition of hydrazine.[40] The structure of $Ru_4(NH)(PhCCPh)(CO)_{11}$ can serve as a model for an NH group bound to a fourfold site, just as the recent structures with μ_3-NH ligands[9,13-16] model imido groups binding to threefold surface sites.

Acknowledgment. This research was supported by a grant (CHE-8410999) from the National Science Foundation.

Registry No. I, 92845-78-8; V, 100927-92-2; diphenylacetylene, 501-65-5; Ru, 7440-18-8.

Supplementary Material Available: Listings of crystallographic data, the positional and thermal parameters, and the structure factors (31 pages). Ordering information is given on any current masthead page.

---

(34) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1417.

(35) Mason, R.; Thomas, K. M. *J. Organomet. Chem.* **1972**, *43*, C39.

(36) Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L.; Tavanaiepour, I.; Abdel-Mequid, S.; Day, V. W. *Inorg. Chem.* **1981**, *20*, 3230.

(37) Dahl, L. F.; Smith, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 2450.

(38) Heveldt, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 340.

(39) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(40) Czaka, A.; Aika, K. *Catal. Sci. Technol.* **1981**, *3*, 87.

On the Bonding of Methyl Groups in Dinuclear Complexes: Terminal, Symmetrically Bridging, or Asymmetrically Bridging?

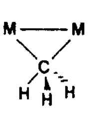
Bruce E. Bursten*[1] and Roger H. Cayton

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

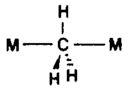
Received January 3, 1986

Summary: The electronic factors leading to the bridging of methyl ligands in dinuclear complexes have been investigated by using Fenske-Hall molecular orbital calculations. $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}Me)^+$ (Cp = η^5-C_5H_5), which contains an agostic, asymmetrically bridging methyl group, is found to have a favorable interaction between one of the methyl C-H bonds and the iron atom to which the methyl group is not terminally bound. The asymmetric methyl bridge is slightly favored over a nonagostic, symmetric bridge for the Fe dimer.

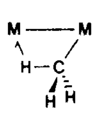
The recognition that alkyl ligands in polynuclear complexes can bond in bridging as well as terminal fashion has resulted in much research into the synthesis and reactivity of complexes containing bridging alkyl ligands. The methyl moiety is known to adopt at least three types of bridging conformations: a symmetric pyramidal bridge (**1**),[2] a symmetric planar bridge (**2**),[3] and an asymmetric bridge (**3**).[4] Casey et al. prepared one of the first dimers containing an asymmetric methyl bridge (**5**) via protonation of the corresponding methylene-bridged complex **4** (eq 1).[4b] This type of bridge is of particular interest in that it contains an agostic M···H···C interaction which represents a possible intermediate in C-H bond activation processes.[5] Although this class of compounds is rapidly growing, little is known about the electronic demands which lead to their formation. In this communication we report the first theoretical description of an agostic methyl-bridged dimer, using **5** as our model. Further, it will be shown that for this system the asymmetric bridge is preferred over either a terminal or symmetrically bridging methyl ligand.



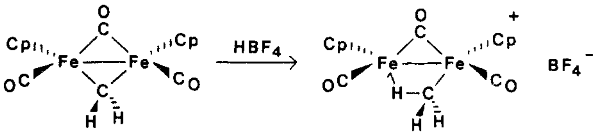
1



2



3



4 **5** (1)

The calculations were performed by using the Fenske–Hall molecular orbital method.[6] Figure 1 depicts the

---

(1) Camille and Henry Dreyfus Foundation Teacher-Scholar (1984–1989) and Fellow of the Alfred P. Sloan Foundation (1985–1987).

(2) (a) Kruger, C.; Sekutowski, J. C.; Berke, H.; Hoffmann, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978** *33B*, 1110–1115. (b) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61. (c) Holton J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425–426. (d) Hursthouse, M. B.; Jones, R. A.; Malik, K. M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128–4139 (e) Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 911–912. (f) Edwards, P. G.; Mertis, K.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 334–344.

(3) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. (b) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 629. (c) Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050–4051.

(4) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–5226. (b) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136. (c) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, *41*–43. (d) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 14–17. (e) Jeffery, J. C.; Orpen, A. G.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1986**, 173–186.

(5) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

(6) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

0276-7333/86/2305-1051$01.50/0