

Communications

Facile Exchange of Naphthalene for η^4 -Benzene in $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$

Voon S. Leong^{1a} and N. John Cooper^{*1,2}

Department of Chemistry, Harvard University

Cambridge, Massachusetts 02138, and

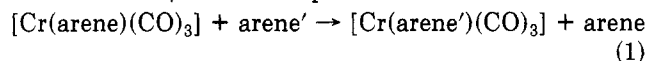
Department of Chemistry, University of Pittsburgh

Pittsburgh, Pennsylvania 15260

Received March 7, 1988

Summary: The η^4 -benzene in $\text{K}_2[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]$ ($\text{K}_2\mathbf{2}$) exchanges with free naphthalene at room temperature to give $[\text{Cr}(\eta^4\text{-C}_{10}\text{H}_8)(\text{CO})_3]^{2-}$ ($\mathbf{5}^{2-}$), as established by oxidation to $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_8)(\text{CO})_3]$ ($\mathbf{4}$), ^1H NMR observation, and protonation to $[\text{Cr}(\eta^5\text{-C}_{10}\text{H}_9)(\text{CO})_3]^-$ ($\mathbf{6}^-$). 1-Methylnaphthalene and 1,4-dimethylnaphthalene also exchange with $\mathbf{2}^{2-}$ if the corresponding naphthalenide is used as the reductant, and this leads to a single isomer of $[\text{Cr}(\eta\text{-C}_{10}\text{H}_6\text{Me}_2)(\text{CO})_3]$ ($\mathbf{8}$) in which the Cr is bonded to the unsubstituted ring of the naphthalene.

The ability of arenes in $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$ complexes to exchange with added arenes (eq 1) has attracted considerable interest³ since its discovery in 1958.⁴ Earlier work has been reviewed,⁵ and it has been recently confirmed that the exchange reaction typically involves activation by a process in which a haptotropic shift gives an intermediate η^4 -arene complex.⁶



We recently reported⁷ that reduction of $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3]$ ($\mathbf{1}$) with alkali-metal naphthalenides in tetrahydrofuran (THF) at -78°C gives two-electron reduction products proposed to contain the η^4 -arene complex $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ ($\mathbf{2}^{2-}$), as suggested, for example, by protonation of the dianion to give the η^5 -cyclohexadienyl complex $[\text{Cr}(\eta^5\text{-C}_6\text{H}_7)(\text{CO})_3]^-$ ($\mathbf{3}^-$). The presence of an η^4 -arene ligand in $\mathbf{2}^{2-}$ raised the possibility that the dianion might undergo facile arene exchange reactions, and we now wish to report that the benzene ligand in $\mathbf{2}^{2-}$ can be replaced by polycyclic arenes under exceptionally mild conditions as summarized in Scheme I and Table I.

(1) (a) Harvard University. (b) University of Pittsburgh.

(2) Address correspondence to N.J.C. at the University of Pittsburgh.

(3) (a) Strohmeier, W.; Mittnacht, H. *Chem. Ber.* **1960**, *93*, 2085-2086.

(b) Strohmeier, W.; Mittnacht, H. *Z. Phys. Chem. (Munich)* **1961**, *29*, 339-346. (c) Strohmeier, W.; Staricco, E. H. *Ibid.* **1963**, *38*, 315-325. (d)

Strohmeier, W.; Muller, R. *Ibid.* **1964**, *40*, 85-95. (e) Mahaffy, C. A. L.;

Pauson, P. L. *J. Chem. Res., Synop.* **1979**, *126M*, 1752-1794. (f) Zimmer-

merman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *Ibid.* **1980**,

108M, 1289-1296.

(4) Natta, G.; Ercoli, R.; Calderazzo, F.; Santambrogio, F. *Chim. Ind. (Milan)* **1958**, *40*, 1003-1007.

(5) (a) Muettterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.*, **1979**, *178*, 197-216. (b) Muettterties, E. L.; Bleeke, J. R.; Wucher-

erer, J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499-525.

(6) (a) Traylor, T. G.; Stewart, K. L.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**,

106, 4445-4454. (b) Traylor, T. G.; Stewart, K. L. *Organometallics* **1984**,

3, 325-327. (c) Traylor, T. G.; Stewart, K. L.; Goldberg, M. L. *Organometallics*

1986, *5*, 2062-2067. (d) Traylor, T. G.; Stewart, K. L. *J. Am. Chem. Soc.*

1986, *108*, 6977-6985. (e) Traylor, T. G.; Goldberg, M. L. *Organometallics*

1987, *6*, 2413-2416. (f) Traylor, T. G.; Goldberg, M. L. *Organometallics*

1987, *6*, 2531-2536.

(7) Leong, V. S.; Cooper, N. J. *J. Am. Chem. Soc.* **1988**, *110*, 2644-2646.

Table I. Yields^a (%) of $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$ Complexes Obtained Following Naphthalene Exchange in THF with $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ ($\mathbf{2}^{2-}$) and O_2 Oxidation

reductant used to generate $\mathbf{2}^{2-}$	<i>n</i> equiv of naphthalene present ^b	$[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$ product and yield	yield ^a of 1	
K[C ₁₀ H ₈]	2	4	30.8	0.7
K[C ₁₀ H ₈]	7.4	4	35.5	0.5
Na[C ₁₀ H ₈]	2	4	34.0	8.6
Na[C ₁₀ H ₈]	7.3	4	43.3	6.4
K[1,4-C ₁₀ H ₆ Me ₂]	2	8a	14.1	2.1
K[1,4-C ₁₀ H ₆ Me ₂]	7	8a	13.0	2.3
Na[1,4-C ₁₀ H ₆ Me ₂]	2	8a	35.0	12.8
Na[1,4-C ₁₀ H ₆ Me ₂]	10	8a	33.0	9.7
Na[1-C ₁₀ H ₇ Me]	2	7a + 7b	18.3 ^{c,d}	5.9 ^c
K[1-C ₁₀ H ₇ Me]	2	7a + 7b	25.0 ^{c,d}	7.5 ^c

^a Yields are based on the quantity of **1** before reduction, exchange, and oxidation and report $[\text{Cr}(\text{arene})(\text{CO})_3]$ products isolated by solvent removal, extraction into Et₂O, solvent removal, and removal of excess naphthalenes in vacuo at 55 °C. Relative yields of naphthalene complexes and **1** were established by ^1H NMR. ^b When *n* = 2, the only free naphthalene was that generated by the reduction. When *n* > 2, *n* - 2 equiv of the naphthalene was added before the solution was warmed from -78°C . ^c In the case of 1-C₁₀H₇Me an additional Et₂O/pentane recrystallization was used to separate the $[\text{Cr}(\text{arene})(\text{CO})_3]$ products from free 1-C₁₀H₇Me. ^d 3.5:1 mixture with both Na⁺ and K⁺ counterion.

Exchange of arenes with $\mathbf{2}^{2-}$ was monitored by reoxidation to a neutral $[\text{Cr}(\text{arene})(\text{CO})_3]$ complex.⁸ In a typical procedure a solution of $\mathbf{2}^{2-}$ in THF formed by reduction of **1** (0.075 g, 0.35 mmol) with potassium naphthalenide⁹ (4.38 mL, 0.16 M, 2 equiv) at -78°C was placed under an atmosphere of dry oxygen. The solution instantly turned light yellow, and the IR carbonyl stretching absorptions of $\mathbf{2}^{2-}$ were replaced by those of **1** at 1968 and 1890 cm⁻¹. The solvent was removed under vacuum, and the neutral products were extracted into diethyl ether. Naphthalene was removed by sublimation (30 min, 55 °C, 10⁻³ mmHg) to give 0.038 g (0.18 mmol, 50.7%¹⁰) of **1** (^1H NMR).

In sharp contrast with this result, an analogous reaction on the same scale in which the solution of $\mathbf{2}^{2-}$ was warmed to room temperature and left at this temperature for 30 min¹¹ before oxidation yielded 0.028 g (0.106 mmol, 30.3%) of $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_8)(\text{CO})_3]$ (**4**—identified by comparison of its ^1H NMR with that reported in the literature¹²) with carbonyl stretching absorptions at 1960 and 1885 cm⁻¹ in THF. Exchange was largely complete under these conditions (corresponding to a twofold naphthalene excess), and **4** contained only small quantities of **1** (ca. 2.3%—NMR).

(8) It is established that the product of irreversible two-electron reduction of **1** (which may be $\mathbf{3}^-$) can be electrochemically reoxidized to **1**: (a) Desey, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471-476. (b) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951-5953.

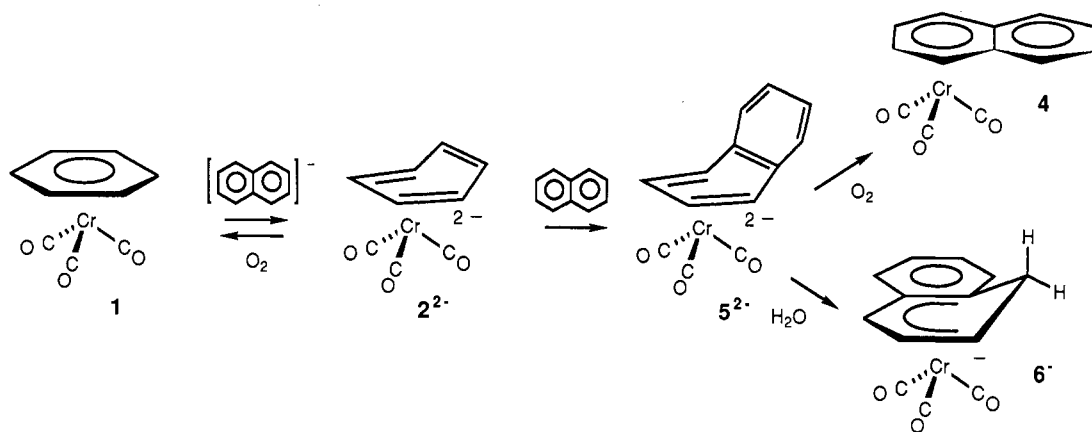
(9) Procedures used in our laboratories for the preparation and standardization of alkali-metal naphthalenide solutions are described in: Maher, J. M.; Beatty, R. P.; Lee, G. R.; Cooper, N. *J. Organomet. Synth.* **1986**, *3*, 35-39.

(10) All yields are based on the quantity of **1** used for reductions.

(11) Thirty minutes at room temperature represents an optimum exchange time—longer periods result in reduced yields, presumably because the η^4 -arene intermediates decompose.

(12) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Ofele, K. *J. Organomet. Chem.* **1967**, *7*, 289-299.

Scheme I

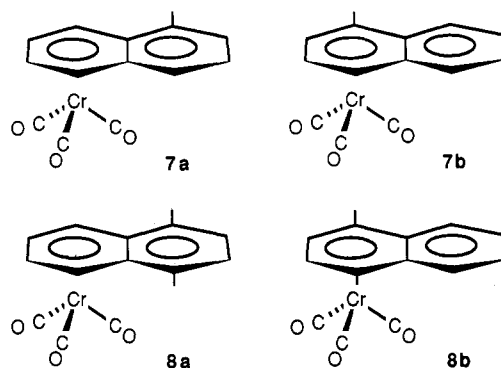


The simplest interpretation (Scheme I) is that naphthalene has been exchanged for the η^4 -benzene in 2^{2-} to form the η^4 -naphthalene complex $[\text{Cr}(\eta^4\text{-C}_{10}\text{H}_8)(\text{CO})_3]^{2-}$ (5^{2-}), previously characterized by Rieke.¹³ Although 5^{2-} is extremely reactive, the η^4 -naphthalene retains more aromatic stabilization than the η^4 -benzene in 2^{2-} , and it is not unreasonable that the exchange should favor 5^{2-} .

The intermediacy of 5^{2-} (which can not be distinguished from 2^{2-} by solution IR) was confirmed by ^1H NMR observation of 5^{2-} in an experiment carried out in THF- d_6 and by a derivatization experiment in which H_2O (6.5 μL , 1 equiv) was added to a solution which had been prepared by reducing 1 (0.075 g, 0.35 mmol) with potassium naphthalenide (4.38 mL, 0.16 M, 2 equiv) at -78°C and allowing the mixture to sit at room temperature for 30 min. The appearance of IR absorptions at 1890, 1788, and 1737 cm^{-1} suggested that the reaction had given the η^5 -cyclohexadienyl complex $[\text{Cr}(\eta^5\text{-C}_{10}\text{H}_9)(\text{CO})_3]^-$ (6^-) reported by Rieke,^{13a} and this was confirmed by isolation of 6^- as analytically pure $[\text{NET}_4]6^-$ (0.05 g, 0.126 mmol, 36%).

The observation of intermediate 5^{2-} rules out alternative mechanisms in which oxidation initiates exchange within a reactive $\text{Cr}(1^-)$ complex, but the report that exchange with 1 can be catalyzed by I_2 ¹⁴ raises the possibility that the reaction is more complex than indicated in Scheme I. Plausible mechanisms can be written in which electron transfer leads to a reactive intermediate such as $[\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3]^-$ which undergoes exchange and is then rereduced, and current data do not rule this out.

Surprisingly, the extent of the exchange reaction appeared to be sensitive to the nature of the counterion, and a reaction analogous to that described above in which the 2^{2-} was generated by sodium naphthalenide reduction gave 4 containing 25.3 mol % of 1 (Table I). We do not, however, believe that this reflects any fundamental counterion effect on the arene exchange equilibrium but rather the greater basicity of 2^{2-} with Na^+ counterions in place of K^+ . Solutions of Na_2 are typically contaminated with traces of 3^- , as indicated by its characteristic carbonyl stretching absorptions at 1890, 1790, and 1740 cm^{-1} in THF. Similar absorptions are present in solutions of 5^{2-} prepared by exchange, and, since 3^- would be oxidized to 1, contamination of 2^{2-} by 3^- is the most probable source of the 1 in the recovered 4. Contamination of 2^{2-} by 3^- would also account for the otherwise surprising observation that the extent of exchange is only marginally improved by the

Scheme II. Isomers of Substituted $[\text{Cr}(\eta^6\text{-naphthalene})(\text{CO})_3]$ Complexes

addition of further naphthalene to the reaction mixture before it is warmed from -78°C (Table I).

Exchange of polycyclic arenes for the benzene in 2^{2-} is not limited to naphthalene itself, and we have also, for example, been able to introduce substituted naphthalenes such as 1-methylnaphthalene and 1,4-dimethylnaphthalene by using the corresponding substituted naphthalenide as the reductant (Table I). Yields and selectivity were, however, reduced in these cases, and the $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_7\text{Me})(\text{CO})_3]^{15}$ (7) and $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_6\text{Me}_2)(\text{CO})_3]^{12}$ (8) formed were significantly contaminated by 1.

The reaction with 1,4-dimethylnaphthalene is particularly interesting because 8 is formed as a single isomer (8a—Scheme II) in which the Cr is exclusively bonded to the unsubstituted ring of the naphthalene. The previous thermal syntheses of 8 from $[\text{Cr}(\text{CO})_6]^{12}$ and from 4 led to 64:36 and 70:30¹⁶ mixtures of 8a and 8b respectively, and, despite the low yield, low-temperature exchange with 2^{2-} offers the only promising route to pure 8a.

It is well established that arene substitution is more rapid in complexes of polycyclic arenes than in complexes of mononuclear arenes,^{3,5,17} and this is generally attributed¹⁸ to the relatively favorable energetics of ring slippage

(15) Opiunenko, Yu. F.; Malyugina, S. G.; Ustynyuk, Yu. A.; Ustynyuk, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1986, 1995.

(16) Kundig, E. P.; Perret, C.; Spichiger, S.; Bernardinelli, G. *J. Organomet. Chem.* 1985, 286, 183–200.

(17) (a) Yagupsky, C.; Cais, M. *Inorg. Chim. Acta* 1975, 12, L27–L28. (b) Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* 1975, 16, 27–34. (c) Howell, J. A. S.; Dixon, D. T.; Kola, J. C.; Ashford, N. F. *J. Organomet. Chem.* 1985, 294, C1–C4.

(18) Other factors sometimes cited include the observed slight displacements of the metal from the ring junction carbon atoms in ground-state structures of naphthalene complexes^{19a} and theoretical studies on the intramolecular migrations of the $[\text{Cr}(\text{CO})_3]$ group which suggest that less energy is required to move the $[\text{Cr}(\text{CO})_3]$ away from the ring junction carbons than toward them.^{19b}

(13) (a) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* 1983, 105, 6314–6315. (b) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* 1987, 26, 420–427.

(14) Harrison, J. J. *J. Am. Chem. Soc.* 1984, 106, 1487–1489.

to generate an η^4 -arene intermediate which results from the retention of aromaticity in the noncoordinated rings. Our results indicate that similar effects reverse the direction of the exchange reaction if the η^4 -arene complex is the starting material rather than an intermediate, that the η^4 -benzene in $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ is an exceptionally labile arene ligand, and that reductive activation arene exchange reactions can lead to products which cannot be prepared pure by other routes.

Acknowledgment. We thank the National Science Foundation for financial support through Grant CHE-8722424 to N.J.C.

Registry No. 1, 12082-08-5; 2⁻, 115677-75-3; 4, 12110-37-1; 5²⁻, 57220-00-5; 6⁻, 87136-08-1; $[\text{NEt}_4]_6$, 87145-02-6; 7a, 105063-49-8; 7b, 105063-45-4; 8a, 12111-62-5; $\text{K}[\text{C}_{10}\text{H}_8]$, 4216-48-2; $\text{Na}[\text{C}_{10}\text{H}_8]$, 3481-12-7; $\text{K}[1,4\text{-C}_{10}\text{H}_6\text{Me}_2]$, 60183-86-0; $\text{Na}[1,4\text{-C}_{10}\text{H}_6\text{Me}_2]$, 60183-89-3; $\text{Na}[1\text{-C}_{10}\text{H}_7\text{Me}]$, 3620-00-6; $\text{K}[1\text{-C}_{10}\text{H}_7\text{Me}]$, 115677-76-4.

(19) (a) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* 1967, 50, 1052-1059. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* 1983, 105, 3396-3411.

Nucleophilic Cleavage of the sp^3 Carbon-Oxygen Bond in Alkoxy-carbene Complexes: Conversion of 2-Oxacyclopentylidene Ligands to Pyridinium-Substituted Acyl Ligands

Joseph M. O'Connor* and Lin Pu

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received April 12, 1988

Summary: The cationic carbene complexes $\text{Ir}(\text{CR}=\text{C}(\text{R}')\text{CR}=\text{CR}')(\text{C}(\text{H})\text{C}(\text{H})\text{C}(\text{H})\text{C}(\text{H})\text{O})(\text{PPh}_3)_2(\text{CO})^+\text{BF}_4^-$ [$\text{R} = \text{CO}_2\text{CH}_3$; $\text{R}' = \text{H}$, **1**; $\text{R}' = \text{CH}_3$, **5**] react with pyridine to form the acyl complexes $\text{Ir}(\text{CR}=\text{C}(\text{R}')\text{CR}=\text{CR}')(\text{COCH}_2\text{CH}_2\text{CHR}'\text{NC}_5\text{H}_5)(\text{PPh}_3)_2(\text{CO})^+\text{BF}_4^-$ [$\text{R}' = \text{H}$, **3**; $\text{R}' = \text{CH}_3$, **6**]. The solid-state structure of the novel pyridinium-substituted acyl complex **3** has been determined by X-ray crystallography.

The role of metal carbene complexes in olefin metathesis,¹ in certain olefin polymerizations,² and as synthetic

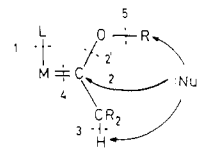


Figure 1.

intermediates³ has generated extensive interest in the properties and reactivity of this prominent compound class. In the area of organic synthesis, 2-oxacycloalkylidene complexes are attractive due to ease of ligand formation,⁴ modification,⁵ and subsequent removal of the metal.⁶ With respect to carbene modification, the isolobal analogy of alkoxy-carbene complexes and esters has been a useful guide for development of carbene reactions.^{7,8a} It is now widely recognized that alkoxy-carbene complexes exhibit four primary reactivity patterns (Figure 1):^{8b} ligand substitution (1), nucleophilic attack at the carbene carbon (2), often resulting in heteroatom exchange (2'), deprotonation at the α -carbon (3), and addition of unsaturated species across the metal-carbon double bond (4). A less commonly observed fifth mode of reactivity is nucleophilic attack at the sp^3 carbon-oxygen bond (5).⁹⁻¹¹

(3) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1987; Vol. 1. Brookhart, M.; Studabaker, W. B. *Chem. Rev.* 1987, 87, 411. Doyle, M. P. *Chem. Rev.* 1986, 86, 919. Casey, C. P. *React. Intermed. (Wiley)*, 1985, 5, 3. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 587. Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. Dötz, K. H. *Pure Appl. Chem.* 1983, 55, 1689. Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* 1983, 55, 1733. Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic: New York, 1976; Vol. I. Casey, C. P. *Organomet. Chem. Libr.* 1976, 1, 397. Fischer, E. O. *Pure Appl. Chem.* 1970, 24, 407; 1972, 30, 353.

(4) Dötz, K. H.; Sturm, W. *Organometallics* 1987, 6, 1424. Casey, C. P. *J. Chem. Soc., Chem. Commun.* 1970, 1220. Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* 1971, 93, 3554. Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* 1971, 93, 2672. Game, C. H.; Green, M.; Moss, J. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1974, 351. Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* 1974, 73, C28. Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* 1973, 6, 202. Marten, D. F. *J. Chem. Soc., Chem. Commun.* 1980, 341. Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* 1980, 33, 2605. Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* 1973, 47, C17. Oguro, K.; Wada, M.; Okawara, R. *J. Organomet. Chem.* 1978, 159, 417. Chisholm, M. H.; Clark, H. C. *J. Chem. Soc., Chem. Commun.* 1970, 763; *Inorg. Chem.* 1971, 10, 1711; *J. Am. Chem. Soc.* 1972, 94, 1532. Dötz, K. H.; Sturm, W. *J. Organomet. Chem.* 1985, 285, 205. King, R. B. *J. Am. Chem. Soc.* 1963, 85, 1922.

(5) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* 1975, 102, 175. Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* 1976, 118, 309. Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* 1977, 16, 3059. Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* 1973, 95, 3552. Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* 1977, 99, 1651. Connor, J. A.; Fischer, E. O. *J. Chem. Soc., Chem. Commun.* 1967, 1024.

(6) Fischer, E. O.; Riedmüller, S. *Chem. Ber.* 1974, 107, 915. Fischer, H. *J. Organomet. Chem.* 1981, 219, C34. Fischer, H.; Zeuner, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1983, 38B, 1365. Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* 1975, 895.

(7) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 711.

(8) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987; p 51. (b) *Ibid.*, p 783.

(9) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* 1972, 94, 9237. Cutler, A. R. *J. Am. Chem. Soc.* 1979, 101, 604. Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* 1967, 10, 188. Green, M. L. H.; Mitchard, L.; Swanwick, M. *J. Chem. Soc. A* 1971, 794. Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* 1975, 88, 199. Chisholm, M. H.; Clark, H. C.; Johns, W. S.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* 1975, 14, 900. Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* 1987, 109, 7688.

(1) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley: New York, 1986. Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983. Grubbs, R. H. In *Comprehensive Organometallic Chemistry: The Synthesis, Reactions and Structures of Organometallic Compounds*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. 8, pp 499-551. Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* 1980, 8, 73. Katz, T. J. *Adv. Organomet. Chem.* 1977, 16, 283.

(2) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* 1987, 109, 4880 and references therein. Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* 1985, 107, 2182. Green, M. L. H. *Pure Appl. Chem.* 1978, 50, 27. Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* 1983, 105, 4942.