

¹H-coupled ¹³C spectrum reveals them as triplets with ¹J_{C-H} = 164 Hz.

As seen with the Me₃SiH reactions, longer reaction times yield methoxysilanes, Me₂RSiOCH₃ (~3 equiv of methoxide species after 9 days at 40 °C), as the final reduced carbon products.¹⁶ The predominant methoxysilane obtained in this system is Me₂HSiOCH₃.²⁰ For this compound, the methoxy proton resonance appears at δ 3.26 ppm and is split by 142 Hz when ¹³CO₂ is used in the reaction. Two additional methoxysilane compounds are also formed and are observed directly by the methoxy proton and carbon resonances.²¹ This is shown in Figure 1 with the ¹H NMR spectra of both the ¹²CO₂ and ¹³CO₂ reactions after 2 weeks, indicating the CO₂-derived methoxy groups present. The methyl groups directly bound to silicon and the various dimethylsiloxanes that are formed as the oxygen acceptors are not directly identified by ¹H NMR, as this region of the spectrum becomes a complicated collection of singlets and multiplets.

Reactions with other silanes are still being investigated. Et₂SiH₂ shows CO₂ reduction chemistry similar to that of Me₂SiH₂ with the exception of slightly slower reaction times. Future studies will involve the reactions of primary silanes in order to investigate the possibilities of branched oligomers and faster rates of reduction.

From this study we have demonstrated that CO₂ can be reduced under very mild conditions to the methoxide level by alkylsilanes. This is closely related to the reduction of CO₂ to methanol by H₂ in that hydrolysis of the final reaction mixtures yield siloxanes and methanol. In these reactions, the silanes serve as both reducing agent and oxygen atom acceptor, driving the reaction through the formation of Si-O bonds.

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(20) Me₂HSiOCH₃: ¹H NMR δ 4.79 (m, 1 H), 3.26 (s, 3 H), 0.08 (d, 6 H). Me₂HSiO¹³CH₃: J_{C-H} = 142 Hz; ¹³C[¹H] NMR, methoxy carbon at 50.2 ppm.

(21) These methoxy groups appear at δ 3.35 and 3.34 in the ¹H NMR and become split by 142 Hz when ¹³CO₂ is used. ³¹C[¹H] NMR: additional resonances at 49.7 and 48.5 ppm.

Highly Reactive Dihydrogen Complexes of Ruthenium and Rhenium: Facile Heterolysis of Coordinated Dihydrogen

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Summary: The moderately stable cationic dihydrogen complexes [(η-C₅Me₅)Ru(CO)₂(η²-H₂)]BF₄ and [(η-C₅Me₅)Re(CO)(NO)(η²-H₂)]BF₄ have been prepared by protonation of the corresponding neutral hydrides. These are the first examples of dihydrogen complexes not containing phosphine coligands to be characterized by NMR methods. The coordinated dihydrogen ligand in these complexes is highly activated toward heterolytic cleavage, as demonstrated by deprotonation with very weak bases such as Et₂O. The estimated pK_a value for coordinated H₂ in the rhenium complex is -2 (CH₂Cl₂).

Since the initial discovery by Kubas,¹ transition-metal dihydrogen complexes have been intensively studied.² Although some understanding of the factors favoring H₂ coordination rather than the more commonly observed oxidative addition of H₂ is beginning to emerge, the ligand systems employed successfully to date in stabilizing H₂ complexes are extremely limited in scope. Virtually all isolable H₂ complexes reported to date contain tertiary phosphine ligands. Calculations seem to indicate that mixtures of σ-donor and strong π-acceptor coligands are optimal for H₂ binding, particularly when an acceptor ligand (such as CO) is trans to H₂.³ In addition to the isolable complexes, there are several examples of dihydrogen complexes which have been characterized only by infrared spectroscopy at very low temperatures. Complexes containing only acceptor ligands, such as Cr(CO)₅(η²-H₂), are observable in significant concentrations only in liquid Xe at ca. 220 K.⁴ Also characterized in liquid Xe are Fe(CO)(NO)₂(η²-H₂) and Co(CO)₂(NO)(η²-H₂), the only reported examples of dihydrogen complexes containing NO ligands.⁵

We have previously reported the synthesis and properties of complexes such as [(η-C₅H₅)Ru(PR₃)(CO)(η²-H₂)]BF₄ (PR₃ = PMe₃, PPh₃, PMe₂Ph, and PCy₃). In the case of the PCy₃-containing complex, an equilibrium between the dihydrogen complex and a small amount of the dihydride complex was observed,⁶ demonstrating that the more basic metal center favors the oxidative addition reaction. We now report the preparation of moderately stable phosphine-free dihydrogen complexes of ruthenium and rhenium and some preliminary studies of their reactivity.

Protonation (HBF₄·Et₂O, 1.2 equiv) of the neutral hydride (η-C₅Me₅)Ru(CO)₂H⁷ in dichloromethane at 220 K affords [(η-C₅Me₅)Ru(CO)₂(η²-H₂)]BF₄ (1).¹¹ Formulation of 1 as a dihydrogen complex is based on the observation of ¹J_{H-D} = 32 Hz in the H-D derivative.¹² Complex 1 was

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Waserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451-452.

(2) For a comprehensive account of the development of this field, see: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-128. Since the review by Kubas several additional dihydrogen complexes have been reported: (a) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598-599. (b) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546-548. (c) Esteruelas, E. S.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563-1564. (d) Hampton, C.; Cullen, W. R.; James, B. R.; Charland, J. *J. Am. Chem. Soc.* **1988**, *110*, 6918-6919. (e) Cotton, F. A.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1277-1278. (f) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19-C22. (g) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725-8726. (h) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 757-758.

(3) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705-710 and references therein.

(4) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645-3651.

(5) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547-2552.

(6) Heinekey, D. M.; Chinn, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5865-5867.

(7) We have prepared (η-C₅Me₅)Ru(CO)₂H by NaBH₄ reduction of (η-C₅Me₅)Ru(CO)₂Br.⁸ The deuteride was prepared by reduction with NaBD₄. This hydride has been previously reported as one of the products of reduction of the cation [(η-C₅Me₅)Ru(CO)₃]BF₄⁹ and from protonation of K[(η-C₅Me₅)Ru(CO)₂].¹⁰

(8) Efraty, A.; Elbaze, G. *J. Organomet. Chem.* **1984**, *260*, 331-334.

(9) Nelson, G. O. *Organometallics* **1983**, *2*, 1474-1475.

(10) Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C18-C22.

(11) ¹H NMR of 1 (CD₂Cl₂, δ, 195 K): 2.07 (s, 15 H), -5.69 (s, 2 H).

(12) The H-D derivative was prepared by protonation of (η-C₅Me₅)Ru(CO)₂D. Due to facile intermolecular proton exchange, a statistical mixture of 1-d₀ and 1-d₁ was observed immediately, even when protonation was carried out at 190 K.

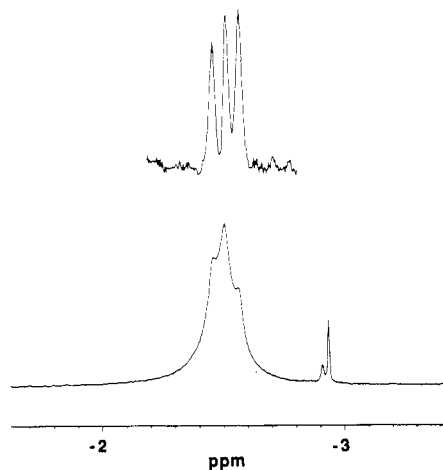
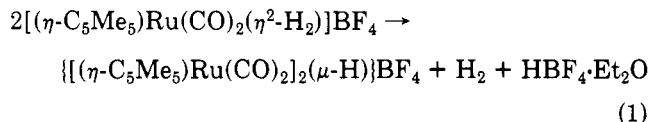


Figure 1. Proton NMR (hydride region) of a mixture of **2** and **2-d₁** at 195 K (CD₂Cl₂, 500 MHz). The lower trace is the normal spectrum showing the resonances due to **2a** (broad singlet) and **2a-d₁** (1:1:1 triplet, ¹J_{H-D} = 27 Hz) overlapping at -2.53 ppm. The resonances due to **2b** and **2b-d₁** are at -2.933 and -2.906 ppm, respectively. The upper trace is the spectrum of **2a-d₁** collected by using a 180-τ-90 pulse sequence with τ = 3 ms. Under these conditions, the signal due to **2a** is nulled.

not isolable at room temperature, since it is unstable with respect to loss of H₂ at temperatures as low as 235 K, leading to formation of the known¹³ dinuclear hydride-bridged dimer **3** (eq 1). Hydride-bridged dimers similar



to **3** have been previously reported as arising from reactions of metal hydrides with trityl cation.^{14,15} These reactions likely proceed via intermediate triphenylmethane complexes, which have been characterized by Sweet and Graham.¹⁶

Although the protonation of the neutral hydride is apparently complete with a slight excess of acid, the reaction of eq 1 strongly implies that there is some equilibrium operational by which **1** is deprotonated by Et₂O to give the neutral hydride, which then can act as a "ligand" to trap the ligand-deficient cation¹⁷ that results from H₂ loss from **1**. Irreversible formation of the stable hydride bridged dimer drives this reaction to completion. Activation of H₂ toward heterolysis by coordination to a cationic metal center is well-precedented. We have previously reported⁶ that pK_a = 17.6 (CH₃CN) for [(η-C₅H₅)CpRu(dmpe)(η²-H₂)]BF₄ (dmpe = 1,2-bis(dimethylphosphino)ethane), but the acidity of **1** must be substantially enhanced in comparison to the dmpe complex (vide infra).

(13) Stasunik, A.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C56-C62.

(14) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214-1222.

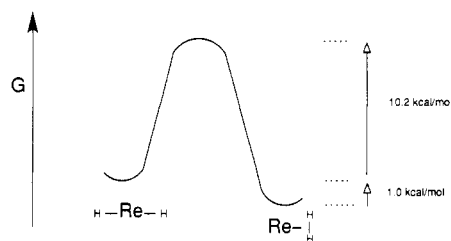
(15) Legzdins, P. A.; Haines, B. W. *Organometallics* **1982**, *1*, 116-124.

(16) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135-140.

(17) The precise nature of this intermediate has not been determined. Two possibilities are a dichloromethane complex and a BF₄⁻ complex. Strong evidence for formation of a dichloromethane complex rather than a BF₄⁻ complex has been reported by Gladysz and Fernández in the closely related (η-C₅H₅)Re(PPh₃)(NO)⁺ system.¹⁸

(18) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207-219.

Scheme I



Protonation of (η-C₅Me₅)Re(CO)(NO)H¹⁹ with HBF₄·Et₂O (CH₂Cl₂ or CD₂Cl₂, 195 K) gives a mixture of two species which are identified as [(η-C₅Me₅)Re(CO)(NO)(η²-H₂)]BF₄ (**2a**) and [(η-C₅Me₅)Re(CO)(NO)H₂]BF₄ (**2b**) (see Figure 1).²¹ The identification of **2a** as a dihydrogen complex is based on the ¹J_{H-D} value of 27 Hz observed for the H-D complex. As expected, the dihydride form **2b-d₁** exhibits no resolvable H-D coupling (see Figure 1). The ratio of **2a:2b** at 225 K is (93 ± 2):(7 ± 2). The chemistry of **2** is similar to that described above for **1**. At 253 K and above, **2** decomposes according to eq 2 to give



the hydride-bridged dimer [(η-C₅Me₅)Re(CO)(NO)]₂(μ-H)⁺ (**4**), which was identified spectroscopically.²² When **2** is prepared by protonation of the neutral hydride with triflic acid, similar H₂ loss occurs, but the intermediate is trapped to give a stable triflate complex, (η-C₅Me₅)Re(CO)(NO)-OSO₂CF₃, which has been fully characterized.²³ The triflate complex reacts with H₂ (40 psi, 195 K) to completely regenerate **2**. A similar displacement of triflate to give a dihydrogen complex has been reported by Bianchini and co-workers.²⁵

An approximate indication of the acidity of **2** was obtained by reaction of **2** with ca. 50 equiv of Et₂O at 190 K. Complete deprotonation to the neutral hydride precursor was observed. The interpretation of pK_a values in solvents such as dichloromethane is somewhat ambiguous, but the pK_a of Et₂OH⁺ is reported to be -2.6 in aqueous sulfuric acid.²⁶ Thus the pK_a of **2** is approximately -2. It seems clear that the susceptibility to heterolytic cleavage

(19) (η-C₅Me₅)Re(CO)(NO)H has been briefly reported.^{20a} This hydride was prepared by reaction of [(η-C₅Me₅)Re(CO)₂(NO)]BF₄^{20a} with triethylamine/acetone/water following the procedure for (η-C₅H₅)Re(CO)(NO)H.^{20b} ¹H NMR (δ, CD₂Cl₂): 2.23 (s, 15 H), -7.59 (s, 1 H). IR (heptane, cm⁻¹): 1958 (ν_{CO}), 1699 (ν_{NO}). The deuteride was prepared by using acetone-d₆ and D₂O.

(20) (a) Graham, W. A. G.; Sweet, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 2811-2815. (b) Graham, W. A. G.; Okamoto, N.; Stewart, R. P. *J. Organomet. Chem.* **1972**, *42*, C32-C34.

(21) ¹H NMR for **2** (δ, CD₂Cl₂): 2.29 (s), 2.40 (s) (ratio 93 ± 2:7 ± 2). These two resonances are due to the methyl groups of **2a** and **2b**, respectively. The hydride signals for these species are shown in the figure.

(22) Complex **4** is a dimer containing two chiral centers which exists as a mixture of two diastereomers, which are designated as *RS,SR* and *RR,SS*. The ¹H NMR spectrum of **4** consists of two sets of signals in the ratio (58 ± 2):(42 ± 2) (δ, CD₂Cl₂): 2.25 (s, 30 H), -13.54 (s, 1 H) and 2.26 (s, 30 H), -12.33 (s, 1 H). The infrared spectrum also indicates the presence of two distinct species in approximately equal amounts. IR (CH₂Cl₂, cm⁻¹): 1996 (s), 1982 (s) (ν_{CO}), 1720 (s, br) (ν_{NO}).

(23) ¹H NMR (δ, CD₂Cl₂): 2.07 (s), IR (CH₂Cl₂, cm⁻¹): 1992 (s) (ν_{CO}), 1724 (s) (ν_{NO}). A related triflate complex (η-C₅H₅)Re(PPh₃)(NO)OSO₂CF₃ has been reported.²⁴

(24) Merrifield, J. A.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022-4029.

(25) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548-5549.

(26) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983-6986.

of the hydrogen molecule has been spectacularly enhanced by coordination to the metal.

The interconversion of **2a** and **2b** was probed by spin saturation transfer experiments at 190 K. Saturation of the methyl resonance of **2b** causes an intensity decrease in the methyl resonance due to **2a**. From these observations, an approximate rate constant of 2.5 s^{-1} was calculated for the conversion of **2b** to **2a**.²⁷ Thus the observed product ratio is clearly a reflection of an equilibrium between **2a** and **2b**, not a kinetic selectivity in the protonation. From the observed product ratio and the spin saturation transfer data, a semiquantitative free energy diagram for the isomers of **2** can be constructed (see Scheme I).

These observations are in marked contrast to the recent report by Gladysz and Fernández¹⁸ that protonation of $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{PPh}_3)(\text{NO})\text{H}$ affords only cationic dihydride complexes, as both cis and trans isomers (with the trans:cis ratio of 60:40 at room temperature). These complexes presumably adopt a distorted capped square pyramid geometry, with the cyclopentadienyl group capping. In this coordination geometry, the terms cis and trans are only approximate descriptors. In the rhenium system described here the replacement of a σ -donor PPh_3 ligand with an effective π -acceptor such as CO presumably renders the metal center much less electron rich, reducing the tendency to oxidative addition. The dihydrogen complex **2a** is thus favored over the dihydride **2b**. An ambiguity remains as to the stereochemistry of the dihydride **2b**. Complex **2b** exhibits only one hydride resonance in the ¹H NMR spectrum. This is consistent with a trans structure or with a highly fluxional cis geometry. The latter possibility is considered less likely since the related cis dihydride $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{PPh}_3)(\text{NO})\text{H}_2\text{BF}_4$ exhibits two hydride resonances in the ¹H NMR, which coalesce only at high temperature ($\Delta G^\ddagger_{295 \text{ K}} = 13 \text{ kcal mol}^{-1}$).¹⁸

Complex **2a** is the first well-characterized example of dihydrogen coordination to a metal center with a nitrosyl coligand. The extraordinary activation of dihydrogen toward heterolysis upon coordination in **1** and **2a** is understandable, since the metal centers involved are strong Lewis acids. Although H₂ is bound only weakly by these acidic metal centers, dihydrogen coordination is still thermodynamically favored over oxidative addition, in contrast to the more basic PPh_3 -containing complexes of Re reported by Gladysz, where oxidative addition is favored.¹⁸ We are continuing to investigate the chemistry of H₂ coordination to Lewis acid metal centers, with particular emphasis on catalysis of isotopic exchange reactions between hydrogen and basic substrates such as water.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A generous loan of ruthenium trichloride by the Johnson-Matthey Co. is gratefully acknowledged.

(27) Proton T_1 values for **2** were determined by using a 180- τ -90 pulse sequence. At 190 K, T_1 values for the hydride resonances in **2a** and **2b** are 5 and 500 ms, respectively. The methyl resonances for both species give a T_1 value of 760 ms. Saturation of the methyl resonance of **2b** causes a decrease in the intensity of the methyl resonance due to **2a** of ca. 15%. The rate constant was calculated as previously outlined for a two-site exchange process.²⁸

(28) Fallor, J. W. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1973; Vol. 5, Chapter 2.

The First Transition-Metal Isonitrilate: Synthesis and Characterization of $\text{K}[\text{Co}(\text{2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_4]$

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Summary: Addition of 4 equiv of 2,6-Me₂C₆H₃NC to $\text{K}[\text{Co}(\text{C}_2\text{H}_4)_4]$ in THF results in ethylene displacement and formation of the homoleptic isonitrilate $[\text{Co}(\text{2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_4]^-$ (**2**), isolated as K_2 , $[\text{K}(\text{DME})]_2$, and $[\text{K}(\text{18-crown-6})]_2$, and formulated as a complex of Co(1-) with terminal isonitrile ligands. Addition of Ph_3SnCl to **2** in THF gave $[\text{Co}(\text{2,6-Me}_2\text{C}_6\text{H}_3\text{NC})_4\text{SnPh}_3]$ (**4**).

Isonitriles, like carbon monoxide, interact synergistically with transition-metal centers, balancing σ donation to the metal from a carbon-based orbital with π back-donation into an antibonding orbital of the isonitrile ligand,¹ and there is an extensive chemistry of transition-metal isonitrile complexes.² It is, however, generally believed, largely on the basis of spectroscopic³ and electrochemical⁴ studies, that isonitriles are better σ donors and poorer π acceptors than CO, consistent with the observation that typical homoleptic isonitrile complexes of many metals are in higher oxidation states than the typical carbonyl complexes of the same metals. In the case of cobalt, for example, a range of stable homoleptic isonitrile complexes of Co(I) have been known for years,⁵ and there is at least one reliable early report of a homoleptic complex of Co(II),⁶ but the first homoleptic Co(0) isonitrile complexes, isoelectronic with $[\text{Co}_2(\text{CO})_8]$, were not reported until 1977,⁷ and there are no reports of isonitrile analogues of $[\text{Co}(\text{CO})_4]^-$ nor indeed of any other transition-metal isonitrilates.⁸

The mild description of Co(0) isonitrile complexes as "air-sensitive even in the solid state"^{7c} and the accessibility of Co carbonyls in oxidation states as low as -3⁹ suggested that cobalt isonitrilates should be synthetically accessible.

(1) 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 148.

(2) This has been systematically reviewed at several stages of development: (a) Malatesta, L. *Prog. Inorg. Chem.* **1959**, *1*, 283. (b) Malatesta, L.; Bonati, F. *Isoyanide Complexes of Transition Metals*; Wiley: New York, 1969. (c) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21. (d) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. (e) Singleton, E.; Oosthuizen, M. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(3) Seminal papers include: Bigorgne, M.; Bouquet, A. *J. Organomet. Chem.* **1963**, *1*, 101. (b) Horrocks, W. D.; Taylor, R. C. *Inorg. Chem.* **1963**, *2*, 723. (c) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702. (d) van Eecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1960. (e) Horrocks, W. D.; Taylor, R. C. *Inorg. Chem.* **1965**, *4*, 584. (f) Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1964**, *97*, 1877. (g) Kruck, Th. *Angew. Chem.* **1967**, *79*, 27.

(4) (a) Treichel, P. M.; Firsich, D. W.; Essenmacher, G. P. *Inorg. Chem.* **1979**, *18*, 2405. (b) Treichel, P. M.; Dirren, G. E.; Mueh, H. J. *J. Organomet. Chem.* **1972**, *44*, 339.

(5) (a) Malatesta, L.; Sacco, A. *Z. Anorg. Chem.* **1953**, *273*, 247. (b) Malatesta, L.; Sacco, A. *Ann. Chim. (Rome)* **1954**, *43*, 617. (c) Sacco, A.; Freni, M. *Angew. Chem.* **1958**, *70*, 599.

(6) Pratt, J. M.; Silverman, P. R. *Chem. Commun.* **1967**, 117.

(7) (a) Barker, G. K.; Galas, A. M. R.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 256. (b) Yamamoto, Y.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *137*, C31. (c) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1978**, *17*, 3111. (d) Carroll, W. E.; Green, M.; Galas, A. M. R.; Murray, M.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 80.

(8) We propose that homoleptic isonitrile complexes of metals in negative oxidation states be termed "isonitrilates" by analogy with metal carbonylates.

(9) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.