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Synthesis of *cis*- and *trans*-Fe(CyNC)$_4$(SPh)$_2$: Bis-thiolate precursors of the mixed-metal complex, (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$

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Abstract

Reaction of [Et$_4$N]$_2$[Fe(SPh)$_4$] with CyNC in MeCN yields *cis*- and *trans*-Fe(CyNC)$_4$(SPh)$_2$ which have been identified by their IR spectral data and physical properties. The less-soluble *trans* isomer converts spontaneously into its *cis* analog in MeCN by a first order process with $k_{obs} = 1.5 \times 10^{-4}$ s^{-1} at 20 °C. Cyclic voltammetry studies show that the *trans* isomer undergoes clean, pseudoreversible, one-electron oxidation with $E_{1/2} = -0.28$ V, while *cis*-Fe(CyNC)$_4$(SPh)$_2$ is oxidized in a multistep, irreversible process at more positive potentials. Both forms of Fe(CyNC)$_4$(SPh)$_2$ react with the substitution-labile carbonylmolybdenum(0) species, (norbornadiene)Mo(CO)$_4$, to generate the new binuclear mixed-metal complex (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$. Cyclic voltammetry of the hetereometallic species shows two pseudoreversible oxidative redox events which formally correspond to Fe^{II}/Fe^{III} and Mo^0/Mo^I couples.

Introduction

Because of our interest in heterometallic compounds containing iron, molybdenum, and sulfur, we have recently developed rational synthetic methods for the preparation of bi- and poly-nuclear thiolate-bridged species containing these elements [1–4]. As part of this program, we have reported the reaction of Mo(RNC)$_4$(S-t-Bu)$_2$ with iron halides to form Mo(RNC)$_4$(S-t-Bu)$_2$FeX$_2$ [1], and

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the reactions of $[Mo(CO)_4(SR)_2]^{2-}$ [2] and $[Mo_2(CO)_8(SR)_2]^{2-}$ [3] with iron and cobalt halides [4] to form $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co). The latter heterometallic species can also be obtained [4] from reaction of $[Et_4N]_2[M(SPh)_4]$ (M = Fe, Co) with $(C_7H_8)Mo(CO)_4$ (C_7H_8 = norbornadiene). As an extension of this general theme, we were also led to explore the chemistry of iron bis-thiolate species which, like their molybdenum analogs, could be used to form mixed-metal complexes with thiolate bridges. This paper reports on the reaction of $[Et_4N]_2[Fe(SPh)_4]$ with cyclohexyl isonitrile (CyNC) to form $Fe(CyNC)_4(SPh)_2$, and on the ability of this compound to act as a precursor to the iron-molybdenum complex $(CyNC)_4Fe(SPh)_2Mo(CO)_4$.

Experimental section

General procedures. All operations were carried out under an inert atmosphere using Schlenk tube and drybox techniques. The compounds $[Et_4N]_2[Fe(SPh)_4]$ [5] and $(C_7H_8)Mo(CO)_4$ (C_7H_8 = norbornadiene) [6] were prepared by literature methods. Cyclohexyl isonitrile (CyCN) was purchased from Aldrich. Acetonitrile (MeCN) was distilled over CaH_2; other reagent grade solvents were used as obtained. Infrared spectra was obtained with a Beckman IR-20A spectrophotometer using KBr pellets prepared in a drybox. Principal peaks are given in wavenumbers. Electronic spectra were recorded on a Cary 118C instrument. Absorption maxima are given in nm with molar absorptivities in parentheses. CO determinations and cyclic voltammetric measurements were carried out as previously described [3]. Potentials are reported relative to the SCE electrode. Elemental analyses were performed in-house with a Perkin–Elmer 240 analyzer equipped with a Microjector from Control Equipment Corp.

Preparation of cis- and trans-Fe(CyNC)$_4$(SPh$_2$). A sample of $[Et_4N]_2[Fe(SPh)_4]$ (1.00 g, 1.33 mmol) was dissolved in MeCN (40 ml) and CyNC (0.61 ml; 5.89 mmol) was syringed into the flask. The mixture was stirred for 20 min and then filtered to obtain 0.28 g (29%) of the flesh-colored *trans* isomer, solutions of which are red-purple. Anal. Found: C, 65.61; H, 7.71; N, 7.44. $C_{40}H_{54}N_4S_2Fe$ calcd.: C, 67.57; H, 7.67; N, 7.88%. IR: 2105(s) (ν(NC)); 1585(m) (ν(NC)) cm^{-1}. VIS (in toluene at 20 ° C): 475 (410); 550 sh (350) nm. Molar absorptivity values are subject to slight error due to the isomerization of the complex as discussed below. However, since the half-life of the reaction is relatively long (ca. 80 min), the parameters obtained from the initial spectrum (measured 2–3 min after dissolution) provide a good estimate of the true values.

The filtrate from the original reaction above was evaporated to dryness under vacuum and the residue extracted with toluene (40 ml). After filtration, the extract was concentrated to 25 ml and addition of hexane (25 ml) yielded the *cis* isomer (0.38 g; 40%) as an orange solid. Anal. Found: C, 67.53; H, 7.95; N, 7.66. $C_{40}H_{54}N_4S_2Fe$ calcd.: C, 67.57; H, 7.67; N, 7.88%. IR: 2130(s), 2180(m) (ν(NC)); 1585(m), (ν(SPh)) cm^{-1}. VIS (in toluene at 20 ° C): 453 (890). *cis*-$Fe(CyNC)_4(SPh)_2$ obtained in this way contains a small amount of impurity (probably the *trans* isomer as judged by the visible spectrum). Consistent with this hypothesis, heating the reaction solution to 50 ° C for 1.5 h resulted in isolation of the product whose visible spectrum was identical to the final spectrum obtained in the kinetic studies (vide infra).

Isomerization of $Fe(CyNC)_4(SPh)_2$. An accurately weighed sample of *trans*-$Fe(CyNC)_4(SPh)_2$ was dissolved in 4 ml of solvent (MeCN or toluene) in a sealed spectrophotometer cell at ambient temperature. The visible spectrum was then monitored as a function of time until the spectral changes were complete. Rate constants were obtained manually from the slopes of linear plots of $\ln(A_t - A_\infty)$ vs. time.

Preparation of $(CyNC)_4Fe(SPh)_2Mo(CO)_4$. Samples of either *cis*- or *trans*-$Fe(CyNC)_4(SPh)_2$ (0.50 g; 0.70 mmol) and $(C_7H_8)Mo(CO)_4$ (0.21 g; 0.70 mmol) were stirred in toluene (30 ml) for 30 min. The orange solid (0.55 g, 86%) which precipitated from the solution was isolated by filtration, washed with hexane, and dried under vacuum. An analytical sample was prepared by recrystallization from CH_2Cl_2/hexane. Anal. Found: C, 56.93; H, 5.82; N, 5.91. $C_{44}H_{54}N_4O_4S_2FeMo$ calcd: C, 56.36; H, 5.82; N, 6.23%. IR: 2200(m), 2155(s) ν(NC) cm^{-1}; 1995(m), 1910(s), 1885(s), 1830(s) (ν(CO)); 1590(w) (ν(SPh)) cm^{-1}. VIS (in CH_2Cl_2 at 20 °C): 360 (583). Percent CO by decomposition with $[NH_4]_2[Ce(NO_3)_6]$: Two analyses gave 98 and 108% of the expected value. Use of Cl_2 or Br_2 as oxidants gave values which were low by 20–30%. In a separate experiment the amount of CO evolved during the synthetic procedure was measured and found to be negligible (ca. 1% of total), substantiating the presence of four carbonyls in the product.

Results and discussion

Synthesis and characterization of $Fe(CyNC)_4(SPh)_2$. The complex $[Et_4N]_2[Fe(SPh)_4]$ was originally reported over ten years ago by Holah and Coucouvanis [7], but its reactivity has not been extensively explored, aside from its role in the iron-thiolate cluster self-assembly reactions studied by Holm et al. [5] who also published a more convenient synthesis for this complex. The formal similarity between $[Fe(SPh)_4]^{2-}$ and $Mo(S\text{-}t\text{-}Bu)_4$ [8] suggested that their chemical reactivities might share some features, and the molybdenum(IV) thiolate compound has been shown to react with π-acceptor ligands to form a variety of complexes [8,9]. In the case of reaction with isocyanides, the molybdenum(II) compound $Mo(RNC)_4(S\text{-}t\text{-}Bu)_2$ can be obtained via a reductive elimination of two of the thiolates [8,9], but because of the relative stability of the iron(II) oxidation state, contrasting with molybdenum(IV), it was not expected that ligand substitution would be accompanied by a redox reaction. Indeed, the reaction between $[Et_4N]_2[Fe(SPh)_4]$ and CyNC in MeCN, resulted in the facile substitution of two of the thiolate groups and addition of four RNC ligands to form $Fe(CyNC)_4(SPh)_2$ (eq. 1).

$$[Et_4N]_2[Fe(SPh)_4] + 4\ CyNC \rightarrow Fe(CyNC)_4(SPh)_2 + 2\ [Et_4N][SPh] \qquad (1)$$

Two forms of the product were obtained: (1) a flesh-colored powder which is only slightly soluble in MeCN and (2) an orange crystalline solid which is much more soluble in this solvent. This difference in solubility provided a convenient method of separating the two products from the reaction mixture. The elemental analyses of the two species are essentially the same [10*], and data from previous studies of the $Fe(RNC)_4X_2$ (X = halide) system indicate that they are likely to be the *trans* and *cis* isomers, respectively, of $Fe(CyNC)_4(SPh)_2$ [11,12]. Thus, the IR

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* This and other references marked with asterisks indicate notes occurring in the list of references.

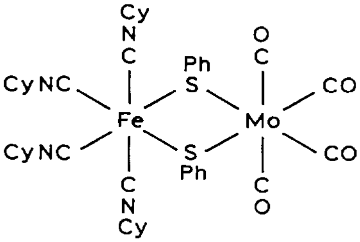
spectra of *cis*-Fe(RNC)$_4$X$_2$ species contain either two (X = I) or three (X = Cl, Br) bands in the NC region, while the spectra of the *trans* analogs contain only one band [11]. In addition, the *cis* isomer in the halide system is yellow and soluble in alcohol, while the *trans* isomer is more intensely colored and much less soluble [12], as would be expected in a polar solvent. The IR spectral data (see Experimental Section) and physical properties of our bis-thiolate complexes are thus consistent with the initial precipitate from the reaction mixture (which is flesh-colored in the solid state and red-purple in solution) being *trans*-Fe(CyNC)$_4$(SPh)$_2$ and the orange product obtained from the filtrate being the *cis* analog. In the absence of X-ray diffraction data, the compounds are presumed to be octahedral. In this light, it is noteworthy that Mo(RNC)$_4$(S-t-Bu)$_2$, which is obtained only in the *cis* form, has an unusually large S–Mo–S angle [8,9], an effect which has been attributed to its d^4 configuration [9]. It is likely that the iron analog, with its d^6 configuration, should more closely approach true octahedral bond angles.

Geometrical isomerization. As noted above, the *cis* and *trans* isomers of Fe(CyNC)$_4$(SPh)$_2$ have distinct visible spectra, providing a convenient method of monitoring their possible interconversion. In this way, it was indeed possible to demonstrate that the *trans* form (while stable in the solid state) slowly isomerizes to the *cis* isomer in either MeCN or toluene solution. This result is not surprising, since *trans*-Fe(RNC)$_4$X$_2$ is known to convert spontaneously to its *cis* analog under similar conditions [13]. The rate of isomerization was measured from spectral changes which showed good isosbestic points at 510 and 415 nm and the linearity of plots of ln $(A_t - A_\infty)$ vs. time shows that the process is first order. Rate constants determined at ambient temperature in MeCN ($k = 1.4 \times 10^{-4}$ s^{-1}) and in toluene ($k = 1.5 \times 10^{-4}$ s^{-1}) indicate no significant solvent dependence and the rate of reaction in toluene was only slightly decreased ($k = 1.2 \times 10^{-4}$ s^{-1}) in the presence of a 50-fold excess of CyNC, although the kinetics were not as clean under these conditions. A more detailed study would be required to establish whether the isomerization proceeds at least partially by a ligand dissociation mechanism. For octahedral tetracarbonylmolybdenum derivatives, both intramolecular and dissociative mechanisms have been established for isomerization, depending on the steric properties of the remaining ligands [14].

Electrochemistry. As shown in Fig. 1, both *cis*- and *trans*-Fe(CyNC)$_4$(SPh)$_2$ show oxidative redox activity. At −45 °C in CH$_2$Cl$_2$, the *trans* form exhibits a clean, pseudoreversible oxidation ($E_{1/2} = -0.28$ V, $E_{pc} - E_{pa} = 185$ mV, $i_{pc}/i_{pa} = 0.84$, and $i_{pa}/\nu^{1/2} = 409$ A cm s$^{1/2}$/V mol). Comparison of the current parameter with literature values [4] indicates that the wave is a one-electron process and thus the redox event is likely due to a simple oxidation of Fe^{II} to Fe^{III}. In contrast, at −45 °C in MeCN, the *cis* form exhibits two closely-spaced oxidative waves which are nearly irreversible ($E_{pa} = +0.10$ V and $+0.22$ V). In the electrochemical studies of similar systems involving *cis/trans* isomerism, oxidation has been shown to induce a clean change in geometry [15], but, since neither of the waves in the voltammogram of the *cis* isomer corresponds to that of the pure *trans* isomer, this behavior is probably not relevant to our system. Instead, it seems clear that the oxidized *trans* species is much more thermally stable than its *cis* analog. The difference in stability upon oxidation could be due to a *trans* effect of the thiolate group in the *cis* isomer, promoting loss of RNC and subsequent decomposition. Alternatively, the proximity of the thiolate groups in the *cis* isomer, and the tendency of metal-thiolate complexes to have a delocalized electronic structure, could lead to a ligand-centered oxidation [16] for the *cis* species, with loss of thiolate ligands as disulfide. At room temperature, both isomers exhibit different electrochemical behavior, the *trans* form showing an additional irreversible wave at 0.45 V and the *cis* showing only a single irreversible wave at 0.08 V, a result indicating thermal instability of the oxidized form of both isomers at higher temperature.

Synthesis and characterization of (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$. To test the utility of $Fe(CyNC)_4(SPh)_2$ as a precursor to mixed-metal species, the reaction between the iron-thiolate complex and the substitution-labile $(C_7H_8)Mo(CO)_4$ [6] was studied. The expected reaction, involving simple substitution of norbornadiene by coordinated thiolate, proved to occur for both *cis* and *trans* isomers of the iron species (eq. 2). The fact that the rate of formation of product from the *trans* starting material was qualitatively the same as for the *cis* (and much faster than the rate of *cis*/*trans* conversion noted above) suggests that the molybdenum reactant catalyzes this isomerization, since the product of necessity contains *cis* thiolates. Elemental analytical and CO evolution data for the product are in keeping with eq. 2 and IR spectral data support the formulation and provide some structural information. Thus the IR spectrum of $(CyNC)_4Fe(SPh)_2Mo(CO)_4$ substantiates a *cis* arrangement about Fe in the product since it contains 2 NC bands, similar to *cis*-$Fe(RNC)_4X_2$ (X = halide, SPh). Likewise, the four-band pattern in the carbonyl region is similar to that exhibited by the *cis*-$Mo(CO)_4$ moieties in $[Mo_2(CO)_8(SR)_2]^{2-}$ [3]. Based on these data, the product is postulated to have the following structure in which the metals (formally Fe^{II} and Mo^0) are characterized by 18 electrons in the absence of metal–metal bonding:

$$Fe(CyNC)_4(SPh)_2 + (C_7H_8)Mo(CO)_4 \rightarrow (CyNC)_4Fe(SPh)_2Mo(CO)_4 + C_7H_8 \quad (2)$$



The electrochemistry of the iron-molybdenum complex is also consistent with this formulation. As shown in Fig. 1, the cyclic voltammogram of $(CyNC)_4Fe(SPh)_2Mo(CO)_4$ contains two pseudoreversible oxidative waves ($E_{1/2}$ = +0.17 V and +0.39 V; $E_{pa} - E_{pc}$ for both events = 130 mV). The total current parameter for both waves of 742 A cm $s^{1/2}$/V mol suggests that the voltammogram is due to sequential one-electron transfers corresponding formally to Fe^{II}/Fe^{III} and Mo^0/Mo^I oxidations. Although these voltammetric data can be compared with those for *cis*-$Fe(CyNC)_4(SPh)_2$ and *cis*-$[Mo(CO)_4(SR)_2]^{2-}$ (representing the Fe and Mo portions of the binuclear complex, respectively), assignment of the two redox events on this basis is equivocal. As noted above, the *cis*-Fe^{II} complex is oxidized to Fe^{III} at ca. +0.2 V, while our previous [2] studies of the Mo^0 species show it to be oxidized to Mo^I at significantly more negative potentials (ca. −0.55 V). On this

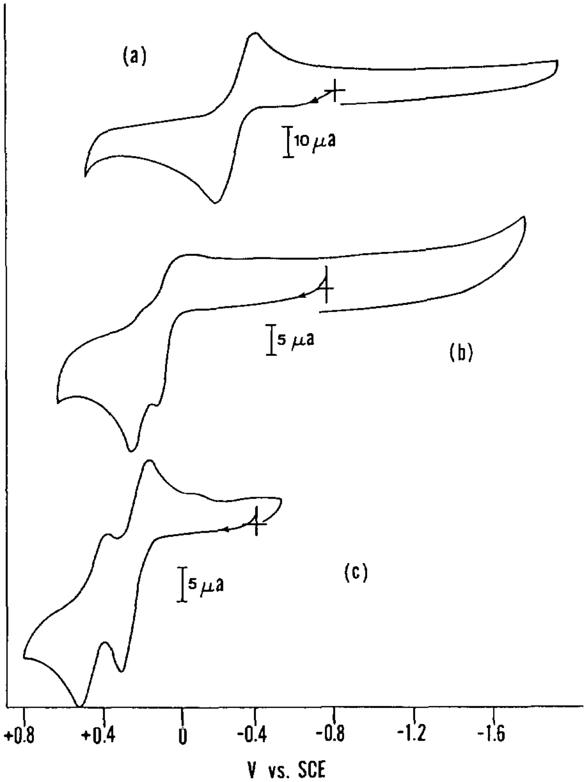


Fig. 1. Cyclic voltammograms of (a) *trans*-Fe(CyNC)$_4$(SPh)$_2$ in CH$_2$Cl$_2$, (b) *cis*-Fe(CyNC)$_4$(SPh)$_2$ in MeCN, and (c) (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$ in CH$_2$Cl$_2$. The scan rate was 50 mV/s and the temperature was −45 °C for all voltammograms.

basis, the more negative oxidation wave for (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$ might be assigned to a formal Mo^0/Mo^I couple and the more positive event to Fe^{II}/Fe^{III} oxidation. However, the dinegative charge on the Mo^0 monomer is likely to make its measured oxidation potential more negative than in a neutral Mo^0 species, making its use in this kind of comparison very questionable.

The fact that the oxidation of this unsymmetric species takes place in sequential one-electron steps rather than via concerted two-electron transfer [17] suggests that, with the proper choice of chemical oxidant, it may be possible to isolate both the 1+ and 2+ analogs of the neutral species. The latter Fe^{III}/Mo^I dication, [(CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$]$^{2+}$ would contain an Fe–Mo bond if each metal is formally characterized by 18 electrons. In addition, the easily-prepared Fe(CyNC)$_4$(SPh)$_2$ may prove to be a useful general reagent for preparation of heterometallic complexes with bis-thiolate bridging units, several examples of which have already been reported [1,4,18].

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References

1 L.D. Rosenhein, J.W. McDonald, and W.E. Newton, Inorg. Chim. Acta, 87 (1984) L33.

2 L.D. Rosenhein, W.E. Newton, and J.W. McDonald, J. Organomet. Chem., 288 (1985) C17.

3 D.A. Smith, B. Zhuang, W.E. Newton, J.W. McDonald, and F.A. Schultz, Inorg. Chem., 26 (1987) 2524.

4 L.D. Rosenhein, W.E. Newton, and J.W. McDonald, Inorg. Chem., 26 (1987) 1695.

5 K.S. Hagen, J.G. Reynolds, and R.H. Holm, J. Am. Chem. Soc., 103 (1981) 4054.

6 R.B. King, Organomet. Synth., 1 (1965) 124.

7 D.G. Holah and D. Coucouvanis, J. Am. Chem. Soc., 97 (1975) 6917.

8 M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu and T. Higuchi, J. Am. Chem. Soc., 103 (1981) 3572.

9 M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Hoshida, and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 5772.

10 Despite several attempts, we were unable to obtain a sample of *trans*-Fe(CyNC)$_4$(SPh)$_2$ which had a completely acceptable carbon analysis. However, the nitrogen and hydrogen percentages agreed closely with the proposed formulation, and the complex converted cleanly into the *cis* isomer and reacted with (C$_7$H$_8$)Mo(CO)$_4$ to form the expected product, i.e. (CyNC)$_4$Fe(SPh)$_2$Mo(CO)$_4$, as discussed in the text. Therefore we believe that this species is formulated correctly despite the slight discrepancy in the carbon analysis.

11 R.C. Taylor and W.D. Horrocks, Inorg. Chem., 4 (1964) 585.

12 L. Malatesta, A. Sacco, G. Padoa, Ann. Chim. (Rome), 43 (1953) 617; Chem. Abstr., 48 (1954) 7476i.

13 M. Pankowski and M. Bigorgne, J. Organomet. Chem., 19 (1969) 393.

14 (a) D.J. Darensbourg, Inorg. Chem., 18 (1979) 14; (b) D.J. Darensbourg and A.H. Graves, ibid., 18 (1979) 1257.

15 For example: (a) R.D. Rieke, H. Kojima, and K. Ofele, J. Am. Chem. Soc., 98 (1976) 6375; (b) A.M. Bond, B.S. Grabaric, and J.J. Jackowski, Inorg. Chem., 17 (1978) 2153; (c) B.P. Sullivan and T.J. Meyer, ibid., 21 (1982) 1037; (d) K.A. Conner and R.A. Walton, Organometallics, 2 (1984) 169.

16 (a) P.M. Treichel, L.D. Rosenhein, and M.S. Schmidt, Inorg. Chem., 22 (1983) 3960; (b) P.M. Treichel and L.D. Rosenhein, ibid., 23 (1984) 4018; (c) A. Winter, G. Huttner, H. Gottlieb, and I. Jibril, J. Organomet. Chem., 286 (1985) 317; d) D.T. Sawyer, G.S. Srivatsa, M.E. Bodini, W.P. Schaefer, and R.M. Wing, J. Am. Chem. Soc., 108 (1986) 936; (e) J.M. Berg, D.J. Spira, K.O. Hodgson, A.E. Bruce, K.F. Miller, J.L. Corbin, and E.I. Stiefel, Inorg. Chem., 23 (1984) 3412.

17 (a) R.E. Ginsburg, R.K. Rothrock, R.G. Finke, J.P. Collman, and L.F. Dahl, J. Am. Chem. Soc., 101 (1979) 6550; (b) J.P. Collman, R.K. Rothrock, R.G. Finke, E.J. Moore, and F. Rose-Munch, Inorg. Chem., 21 (1982) 146; (c) B. Zhuang, J.W. McDonald, F.A. Schultz, and W.E. Newton, Organometallics, 3 (1984) 943 and ref. therein.

18 a) A.R. Dias and M.L.H. Green, J. Chem. Soc. A, (1971) 2807; (b) ibid., (1971) 1951; (c) W.E. Douglas and M.L.H. Green, J. Chem. Soc., Dalton, (1972) 1796; (d) D. O'Hare, M.L.H. Green, and F.G.N. Cloke, J. Organomet. Chem., 282 (1985) 225; (e) N.C. Payne, N. Okura, and S. Otsuka, J. Am. Chem. Soc., 105 (1983) 245; (f) S. Lu, N. Okura, T. Yoshida, S. Otsuka, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 105 (1983) 7470; (g) T.A. Wark and D.W. Stephan, Inorg. Chem., 26 (1987) 363; (h) M. Werner, B. Ulrich, U. Schubert, P. Hofman, and B. Zimmer-Green, J. Organomet. Chem. 297 (1985) 27; (i) P.S. Braterman, V.A. Wilson, and K.K. Joshi, J. Chem. Soc. A, (1971) 191; (j) T.S. Cameron, C.K. Prout, G.V. Rees, M.L.H. Green, K.K. Joshi, G.R. Davies, B.T. Kilbourn, P.S. Braterman, and V.A. Wilson, Chem. Commun., (1971) 14; (k) C.J. Ruffing, T.B. Rauchfuss, Organometallics, 4 (1985) 524.