

within the ~8-ns laser pulse (see Figure 1). A UV absorption increasing in intensity from 300 to 260 nm is also formed within the excitation pulse; however, this band demonstrates no decay or chemical reactivity. This absorption overlaps with the UV absorption band of phenanthrene and is attributed to the "instantaneous" generation of **2**. It must be noted that every effort was made to directly detect :CCl<sub>2</sub> (especially in the 440–560-nm range) by varying the experimental conditions, e.g., precursor concentration, solvent, saturating gases, laser power, and laser configuration. If :CCl<sub>2</sub> has an absorption band in this region,<sup>9</sup> it is "overwhelmed" by the absorptions of triplet phenanthrene.

Recently, Platz and co-workers have demonstrated that ground-state singlet carbenes react with pyridine to form pyridinium ylides,<sup>13</sup> which possess intense absorptions that have successfully been used to competitively measure both the inter- and intramolecular kinetics of several "invisible" alkylchlorocarbenes.<sup>13,14</sup> Similar to the absorption spectra of the pyridinium ylides of methylchlorocarbene ( $\lambda_{\text{max}} = 360 \text{ nm}$ ),<sup>14a</sup> *tert*-butylchlorocarbene<sup>13</sup> ( $\lambda_{\text{max}} = 376 \text{ nm}$ ), benzylchlorocarbene<sup>14b</sup> ( $\lambda_{\text{max}} = 379 \text{ nm}$ ), and cyclopropylchlorocarbene<sup>14c,d</sup> ( $\lambda_{\text{max}} = 370 \text{ nm}$ ), LFP of  $1 \times 10^{-4} \text{ M}$  **1** in the presence of pyridine<sup>15</sup> results in the absorption spectrum of the pyridinium ylide of dichlorocarbene (**4**) having an absorption maximum at 390 nm (see Figure 1).

Again, phenanthrene is "instantaneously" formed,<sup>16</sup> as evidenced by the UV absorption band of **2** (vide supra); however, it is possible to minimize interference from reexcitation of **2** and monitor the absorption of pyridinium ylide **4** in air-saturated C<sub>6</sub>H<sub>12</sub> since there should be no observable reactivity of either singlet :CCl<sub>2</sub> or the zwitterionic ylide **4** with molecular oxygen.<sup>17</sup> Therefore, the bimolecular rate constant for the reaction of :CCl<sub>2</sub> with pyridine,  $k_p$ , ( $7.90 \pm 0.23$ )  $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , is readily obtained (eq 1) by monitoring the pseudo-first-order growth rate of **4**,  $k_{\text{expl}}$ , at various pyridine concentrations,

$$k_{\text{expl}} = k_o + k_p[\text{pyridine}] \quad (1)$$

where  $k_o$  represents the rate of decay of :CCl<sub>2</sub> in the absence of pyridine.<sup>18</sup> The absolute bimolecular quenching rate constants of :CCl<sub>2</sub> with several olefinic substrates (see Table I) are also readily obtained by using the competitive "probe" technique,<sup>19</sup> by monitoring changes in  $k_{\text{expl}}$  at an experimentally optimum concentration of pyridine,<sup>20</sup>  $1.23 \times 10^{-4} \text{ M}$ , with added quencher:  $k_{\text{expl}} = k_o + k_p[\text{pyridine}] + k_q[\text{olefin}]$ .

The absolute kinetic data presented in Table I demonstrate the electrophilic nature of :CCl<sub>2</sub> by the marked decrease in reactivity of :CCl<sub>2</sub> toward olefins of decreasing substitution. The relative rates of :CCl<sub>2</sub> with Me<sub>2</sub>C=CMe<sub>2</sub>, MeCH=CMe<sub>2</sub>, *trans*-MeCH=CHEt, *c*-C<sub>6</sub>H<sub>10</sub>, and CH<sub>2</sub>=CH-*n*-C<sub>4</sub>H<sub>9</sub> have been reported to be 53.7, 23.5, 2.14, 1.00, and 0.19, respectively.<sup>21</sup> It must be noted, however, that the two studies are *not* directly comparable since, in the relative studies, :CCl<sub>2</sub> is generated by alkoxide-induced  $\alpha$ -elimination (–10 to –20 °C), where carbenoid

involvement is possible.<sup>22</sup> Nevertheless, the supporting trends verify the placement of :CCl<sub>2</sub> as an electrophile on the "carbene selectivity spectrum" of Moss.<sup>1</sup> However, it is interesting to point out a discrepancy in the empirical correlation. Namely, the absolute rate constants of :CCl<sub>2</sub> are greater than those measured<sup>23</sup> for Ph $\ddot{\text{C}}\text{Cl}$  (see Table I). Recent experiments<sup>24</sup> have demonstrated, however, a more "amphiphilic" character of Ph $\ddot{\text{C}}\text{Cl}$  with substantial reactivity toward electron-deficient olefins.<sup>25</sup>

In summary, a long-awaited clean photolytic source of :CCl<sub>2</sub> has been presented. Although :CCl<sub>2</sub> still eludes direct observation, the well-documented pyridinium ylide probe technique has been used to successfully measure the first absolute kinetics of this most important carbene.

Currently, other chemical, kinetic, and energetic aspects of :CCl<sub>2</sub> reactivity are being pursued.

**Acknowledgment.** This is Notre Dame Radiation Laboratory Document No. NDRL-3250. We thank the Office of Basic Energy Sciences of the Department of Energy for support and the National Science Foundation for support of the work done at the University of New Hampshire.

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(25) Also, as a referee most correctly pointed out, the high reactivity observed for :CCl<sub>2</sub> is most likely a consequence of a very low LUMO for :CCl<sub>2</sub>, as predicted by FMO theory.<sup>26</sup>

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## Viability of the [Ni<sup>III</sup>(SR)<sub>4</sub>]<sup>–</sup> Unit in Classical Coordination Compounds and in the Nickel-Sulfur Center of Hydrogenases

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Recent vigorous research activity directed at elucidating the structural, reactivity, and physical properties of nickel–thiolate coordination compounds has been prompted by the discovery of a nickel–sulfur center in numerous hydrogenase enzymes.<sup>1</sup> Cumulative chemical and spectroscopic evidence suggests that the nickel in these hydrogenases is capable of catalyzing both the reductive formation and oxidative cleavage of dihydrogen:  $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$ . Nickel EXAFS studies of these hydrogenases suggest that the nickel is coordinated to approximately four sulfurs in either a distorted octahedral or square-pyramidal array.<sup>2</sup> In their isolated states, the nickel-containing hydrogenases exhibit characteristic rhombic ESR spectra which have been assigned to a Ni(III) center.<sup>1</sup> Remarkably, the redox potentials for the Ni(III)/Ni(II) couple of these hydrogenases occur in the range of ca. –0.150 to –0.400 V vs NHE (–0.390 to –0.640 V vs SCE),<sup>1</sup> which is in striking contrast to the more positive values (+0.50 to +1.50 V vs SCE) reported for the Ni(III)/Ni(II) couple of

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(15) Pyridine (Fisher Scientific) was freshly distilled prior to use.

(16) Continuous-flow cells were used in all LFP experiments.

(17) Ylide **4** has a lifetime of ~35  $\mu\text{s}$  and, indeed, demonstrates no reactivity toward O<sub>2</sub>; however, it is quenched by the dipolarophile diethyl fumarate with a rate constant of  $(7.42 \pm 0.20) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

(18)  $k_o$  can only be estimated to be  $\leq 1 \times 10^5 \text{ s}^{-1}$  from the intercept,  $(3 \pm 8) \times 10^4 \text{ s}^{-1}$ , of the pyridine quenching plot.

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(20) Under typical experimental conditions (3-mm sample-cell path length), the OD of pyridine at 266 nm was 0.16, as compared to  $\geq 0.8$  for the OD of precursor **1**. Furthermore, no transient species were detected upon 266-nm LFP of  $1.23 \times 10^{-4} \text{ M}$  pyridine in C<sub>6</sub>H<sub>12</sub>.

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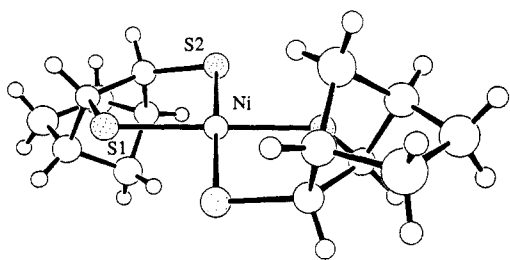


Figure 1. Perspective view of  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$ .

classical coordination compounds.<sup>3</sup>

Problems associated with the synthesis and isolation of stable monomeric Ni(III)-polythiolate complexes as analogues for the nickel-sulfur center in hydrogenases have been attributed to the propensity of nickel thiolates to oligomerize<sup>4</sup> and to the instability of Ni(III)-thiolate species with regard to autoredox decomposition reactions.<sup>5</sup> Herein, we report the synthesis and chemical properties of a stable monomeric Ni(II)-tetrathiolate complex which is readily oxidized to a stable Ni(III)-tetrathiolate species at biologically relevant redox potentials.<sup>6</sup>

The reaction of the dilithium salt of bicyclo[2.2.1]heptane-*exo-cis*-2,3-dithiolate,<sup>7</sup>  $[\text{Li}_2(\text{S}_2\text{-norbornane})]$  (2.5 equiv), with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1 equiv) and  $(\text{Et}_4\text{N})\text{Br}$  (2.5 equiv) in DMF for 24 h at room temperature produced a light green solution, from which a good yield of green microcrystalline  $(\text{Et}_4\text{N})_2[\text{Ni}(\text{S}_2\text{-norbornane})_2]$  was acquired after unexceptional workup. In the absence of precipitating cation, this procedure gave X-ray quality crystals of  $[\text{Li}(\text{DMF})(\text{MeOH})]_2[\text{Ni}(\text{S}_2\text{-norbornane})_2]$  (**1**). The X-ray structure determination<sup>9</sup> of **1** shows the anion (Figure 1),  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$ , to possess a crystallographically imposed center of inversion which requires the four sulfurs to be coordinated to the nickel in a rigorously planar configuration and the two  $[\text{S}_2\text{-norbornane}]^{2-}$  ligands to be oriented in the anti configuration.<sup>10</sup> The  $[\text{NiS}_4]$  unit is a nearly perfect square with the angles  $\text{S1-Ni-S2} = 90.13(6)^\circ$  and  $\text{S1-Ni-S2}' = 89.87(6)^\circ$  and distances  $\text{Ni-S1} = 2.182(2) \text{ \AA}$  and  $\text{Ni-S2} = 2.186(2) \text{ \AA}$ . The lithium ions occur in dimeric units,  $[(\text{MeOH})\text{Li}(\mu\text{-DMF})_2\text{Li}(\text{MeOH})]$ , which link the  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  anions into chains via Li-S coordination.

Although oligomeric nickel alkylthiolate complexes are numerous,<sup>4</sup> monomeric  $[\text{Ni}^{\text{II}}(\text{SR})_4]^{2-}$  complexes of alkylthiolates are rare; beside  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$ ,  $[\text{Ni}(\text{edt})_2]^{2-}$  is the only other example.<sup>11</sup> Since  $[\text{Ni}(\text{edt})_2]^{2-}$  converts to  $[\text{Ni}_2(\text{edt})_3]^{2-}$  and  $(\text{edt})^{2-}$

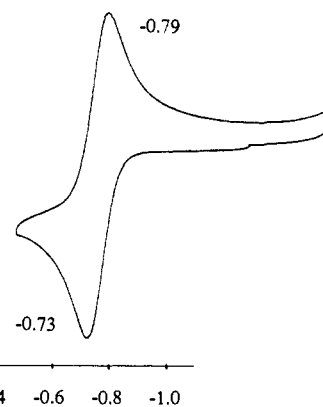


Figure 2. Cyclic voltammetric response (200 mV/s) of  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  in DMF with the indicated peak potentials vs SCE.

readily in protic solvents ( $\text{H}_2\text{O}$ ,  $\text{MeOH}$ ) and slowly in aprotic solvents (DMF),  $[\text{Ni}(\text{edt})_2]^{2-}$  was prepared via a reaction where the ratio of  $\text{edt}^{2-}$  to  $\text{Ni}^{2+}$  is 10:1.<sup>11</sup> In comparison,  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  is more robust. The UV-vis spectra of  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  are similar and appear constant for several hours in both  $\text{MeOH}$  and DMF.<sup>12</sup> The rigid conformation of the S-C-C-S chelating unit in  $(\text{S}_2\text{-norbornane})^{2-}$  may account for the increased stability of  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  with respect to oligomerization reactions.

Electrochemical studies demonstrate that  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  is reversibly oxidized by one electron to a Ni(III) species in DMF (Figure 2). The reversibility of this redox process was established by normal-pulse and reverse-pulse polarography, which gave the  $E_{1/2}$  [slope;  $i(\text{cathode})/i(\text{anode})$ ] of the Ni(III)/Ni(II) couple as  $-0.76 \text{ V vs SCE}$  (61 mV, 0.94).<sup>13</sup> Interestingly, cyclic voltammetric studies of  $[\text{Et}_4\text{N}]_2[\text{Ni}(\text{S}_2\text{-norbornane})_2]$  in  $\text{MeOH}$  show a considerable cathodic (positive) shift of the Ni(III)/Ni(II) couple to  $-0.46 \text{ V vs SCE}$  ( $\Delta E_p = 75 \text{ mV}$ ).<sup>14</sup> These potentials are the lowest ever observed for a nonbiological nickel complex, a situation that is consistent with the observation that thiolates stabilize metals in high formal oxidation states.<sup>15</sup>

When a DMF solution of  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{2-}$  is exposed to air, an immediate color change to red-brown is observed. The ESR spectrum of this solution at 77 K exhibits an axial signal with  $g_{\parallel} = 2.14$  and  $g_{\perp} = 2.05$ , which is consistent with a Ni(III) complex with a  $S = 1/2$  ground state. Moreover, the ESR spectrum remains invariant under different solvent conditions (pyridine, DMF,  $\text{CH}_3\text{CN}$ ) and different methods of oxidation (air,  $[\text{Cp}_2\text{Fe}]^+$ , or controlled potential electrolysis). No hyperfine coupling by  $^{14}\text{N}$  is observed when the oxidations are carried out in  $\text{CH}_3\text{CN}$  or pyridine. An ESR spectrum with  $g_{\parallel} > g_{\perp}$  is consistent with a square-planar Ni(III) complex with the unpaired electron in the  $d_{xy}$  orbital.<sup>16</sup> The cumulative ESR spectral evidence is consistent with the formulation of the oxidized product as  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{1+}$  with no axial ligands. The oxidized complex appears thermally stable; there is no change in the ESR signal intensity of the DMF solutions after standing for 24 h at room temperature. Attempts to isolate and structurally characterize this Ni(III) complex are underway. It should be noted that

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(8)  $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{S}_2\text{-norbornane})_2]$  was synthesized by an analogous reaction using water as the reaction solvent.  $^1\text{H NMR}$  spectral data of  $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{S}_2\text{-norbornane})_2]$  (300 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  0.080 (2 H, dm,  $J = 9 \text{ Hz}$ ), 0.87 (4 H, dm,  $J = 8 \text{ Hz}$ ), 1.24 (4 H, dm,  $J = 8 \text{ Hz}$ ), 1.86 (4 H, br s), 2.69 (2 H, d,  $J = 9 \text{ Hz}$ ), 2.85 (4 H, br s), 7.71 (40 H, m).

(9) Crystal data for **1**: monoclinic,  $C2/c$ ,  $a = 18.245(4) \text{ \AA}$ ,  $b = 9.359(3) \text{ \AA}$ ,  $c = 17.176(6) \text{ \AA}$ ,  $\beta = 101.28(2)^\circ$ ,  $V = 2876(3) \text{ \AA}^3$ ,  $Z = 4$ . Data was collected at room temperature by using molybdenum radiation on a CAD4 diffractometer. Final least-squares refinement with all the non-hydrogens anisotropic gave  $R(R_w) = 0.048(0.057)$  using 1452 observations  $I > 3\sigma(I)$ .

(10) In  $[\text{Co}^{\text{III}}(\text{S}_2\text{-norbornane})_2]^{1+}$ , the ligands are arranged in the anti configuration. In  $[\text{Fe}^{\text{III}}(\text{S}_2\text{-norbornane})_2]^{2+}$ , the two ligands are arranged in the syn configuration; the iron is five coordinate. Fox, S.; Millar, M., unpublished results.

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there is no direct correspondence between the observed  $g$  values measured for  $[\text{Ni}(\text{S}_2\text{-norbornane})_2]^{1-}$  and for the various spectra for the hydrogenase enzymes.<sup>1</sup>

Considerable controversy remains regarding the mechanism by which the nickel might catalyze hydrogenase activity. It has been proposed that during catalysis the nickel shuttles through the Ni(IV), Ni(III), Ni(II), Ni(I), and/or Ni(0) redox levels.<sup>1</sup> Our work suggests that the observed nickel-based redox potentials in hydrogenases are consistent with the Ni(III)/Ni(II) redox couples of a nickel center coordinated with predominantly anionic sulfur ligands.<sup>17</sup>

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**Supplementary Material Available:** Tables of atomic positional and thermal parameters and bond distances and angles for **1** (4 pages); listings of observed and calculated structure factors for **1** (11 pages). Ordering information is given on any current masthead page.

(17) We have recently isolated and determined the structure of  $(\text{Et}_4\text{N})\text{-Li}(\text{MeOH})_3(\text{H}_2\text{O})[\text{Ni}(\text{S}_2\text{-1,2-cyclohexane})_2]$ , which is reversibly oxidized to a Ni(III) species in DMSO at  $E_{1/2} = -0.73$  V vs SCE ( $\Delta E_p = 60$  mV).

## Conjugate Addition of a Chiral Manganese Acetylide Complex to Epoxides, Vinyl Ketones, and Heterocumulenes

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The application of metal-carbene complexes in synthetic organic chemistry is well developed,<sup>2</sup> but one area in need of further exploration is the use of chiral-at-metal carbene complexes in stereospecific syntheses.<sup>3</sup> In an attempt to prepare chiral carbene complexes of the type  $\text{Cp}'(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}(\text{OMe})\text{CHRR}'$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$ ), we have discovered a family of highly nucleophilic and chiral acetylide complexes that undergo a number of interesting addition and cycloaddition reactions with organic substrates.<sup>4,5</sup> The starting point for these studies is the carbene

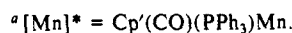
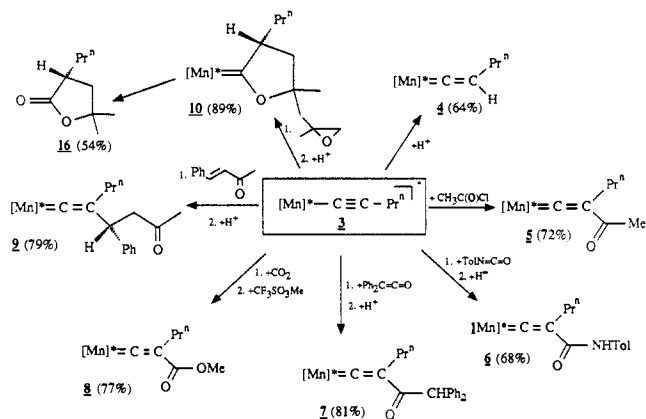
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(2) For a review, see: Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

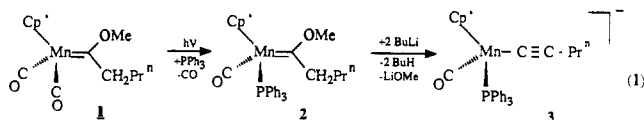
(3) (a) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559. (b) Curtis, P. J.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 747. (c) Baird, G. J.; Davies, S. G.; Jones, R. H.; Prout, K.; Warner, P. *J. Chem. Soc., Chem. Commun.* **1984**, 745. (d) Ayscough, A. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1648. (e) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (f) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (g) Smith, D. E.; Gladysz, J. A. *Organometallics* **1985**, *4*, 1480. (h) *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: New York, 1989; Vol. 3, pp 141-223.

(4) Illustrated herein are reactions for  $[\text{Cp}'(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}(\text{OMe})\text{CHRR}']$  ( $\text{R} = \text{Pr}^n$ ) although similar transformations have been observed for the  $\text{R} = \text{H}$  and  $\text{R} = \text{Me}$  analogues.

## Scheme 1<sup>a</sup>



complex **2**,<sup>6</sup> which was prepared from complex **1** by photosubstitution of  $\text{PPh}_3$  for  $\text{CO}$ , eq 1. It was anticipated that depro-



tonation of the  $\beta$ -carbon of the carbene ligand of **2** with  $\text{BuLi}$  would yield an anionic vinyl complex<sup>8</sup> that upon subsequent addition of  $\text{R}'\text{I}$  would give the desired  $\text{Cp}'(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}(\text{OMe})\text{CHRR}'$ . However, a vinyl complex was not formed upon treatment of **2** with  $\text{BuLi}$ , but instead the anionic acetylide complex **3**<sup>9</sup> was produced, eq 1. Two equivalents of  $\text{BuLi}$  are necessary

(5) For other relevant studies of metal acetylide complexes, see refs 3c, f and see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Nast, H. *Coord. Chem. Rev.* **1982**, *47*, 89. (c) Berke, H. Z. *Naturforsch.* **1980**, *35b*, 86. (d) Bruce, M. I.; Humphrey, M. G.; Matison, J. G.; Salil, K. R.; Seincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955. (e) Bruce, M. I.; Duffy, N. D.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1987**, *335*, 365. (f) Bruce, M. I.; Humphrey, P. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *303*, 417. (g) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *226*, C1. (h) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organometallics* **1988**, *7*, 343. (i) Bruce, M. I. *Pure Appl. Chem.* **1986**, *58*, 553. (j) Bruce, M. I.; Rodgers, J. R.; Snow, M. R.; Swincer, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 271. (k) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 96. (l) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517. (m) Hong, P.; Sonogashira, K.; Hagihara, N. *J. Organomet. Chem.* **1981**, *219*, 363. (n) Hong, P.; Sonogashira, K.; Hagahara, N. *Tetrahedron Lett.* **1970**, 1633. (o) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1979**, *166*, C13. (p) Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturges, M. A. *Organometallics* **1988**, *7*, 2553. (q) Barrett, A. M.; Carpenter, N. E.; Mortier, J.; Sabat, M. *Organometallics* **1990**, *9*, 151. (r) Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1985**, *4*, 2062. (s) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanolini, F. *Organometallics* **1990**, *9*, 241.

(6) Selected data for the new compounds described herein are as follows. **2**: Anal. C, H. IR (THF):  $\nu_{\text{CO}} = 1834$   $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  340.99 (d,  $J_{\text{PC}} = 23.3$  Hz,  $\text{C}(\text{OMe})\text{Bu}^n$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  89.97. **4**: Anal. C, H. IR (THF):  $\nu_{\text{CO}} = 1892$  (s),  $\nu_{\text{C}=\text{C}} = 1633$  (w)  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR: 364.30 (d,  $J_{\text{PC}} = 30.8$  Hz,  $\text{C}=\text{CHPr}^n$ ), 236.67 (d,  $J_{\text{PC}} = 32.2$  Hz, CO), 117.89 (s,  $\text{C}=\text{CHPr}^n$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  93.25. **7**: Anal. C, H. IR (THF):  $\nu_{\text{CO}} = 1913$  (s),  $\nu_{\text{CO}} = 1631$  (w),  $\nu_{\text{C}=\text{C}} = 1545$  (s)  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR:  $\delta$  366.24 (d,  $J_{\text{PC}} = 30.5$  Hz,  $\text{C}=\text{C}(\text{Pr}^n)\text{C}(\text{O})\text{CHPh}_2$ ), 235.88 (d,  $J_{\text{PC}} = 30.5$  Hz, CO), 198.71 ( $\text{C}=\text{C}(\text{Pr}^n)\text{C}(\text{O})\text{CHPh}_2$ ).  $^{31}\text{P}$  NMR:  $\delta$  86.10. **9**: Anal. C, H. IR (THF):  $\nu_{\text{CO}} = 1887$  (s), 1713 (w);  $\nu_{\text{C}=\text{C}} = 1636$  (w)  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR:  $\delta$  361.39 (d,  $J_{\text{PC}} = 24.3$  Hz,  $\text{C}=\text{C}(\text{Pr}^n)\text{CHPhCH}_2\text{C}(\text{O})\text{Me}$ ), 237.64 (d,  $J_{\text{PC}} = 33.1$  Hz, CO), 208.30 ( $\text{C}=\text{C}(\text{Pr}^n)\text{CHPhCH}_2\text{C}(\text{O})\text{Me}$ ).  $^{31}\text{P}$  NMR:  $\delta$  91.85. **10**: Anal. C, H. IR (THF):  $\nu_{\text{CO}} = 1832$   $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR:  $\delta$  334.32 (d,  $J_{\text{PC}} = 28.3$  Hz,  $\text{Mn}=\text{C}$ ), 236.90 (d,  $J_{\text{PC}} = 30.5$  Hz, CO).  $^{31}\text{P}$  NMR:  $\delta$  88.90.

(7) Prepared from  $\text{CpMn}(\text{CO})_2$  and  $\text{BuLi}$  by following the procedure given by Fischer and Maasböl (Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445) for related compounds.

(8) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309.

(9)  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}(\text{R})\text{R}']$ ,  $\text{R} = \text{Me}$ : IR (THF)  $\nu_{\text{CO}} = 2049$  (m),  $\nu_{\text{CO}} = 1779$  (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (THF- $d_6$ )  $\delta$  6.54-6.92 (PPh<sub>3</sub>), 4.12, 3.95, 3.87, 3.81 ( $\text{C}_5\text{H}_4\text{CH}_3$ ), 2.64 (s,  $\text{C}_5\text{H}_4\text{CH}_3$ ), 2.62 (s,  $\text{C}=\text{CCH}_3$ );  $^{13}\text{C}$  NMR (THF- $d_6$ )  $\delta$  238.63 (d,  $J_{\text{PC}} = 33.6$  Hz, CO), 143.9-133.7 (PPh<sub>3</sub>), 112.7 ( $\text{C}=\text{CCH}_3$ ), 97.6, 82.4, 80.8, 80.1, 76.5 ( $\text{C}_5\text{H}_4\text{CH}_3$ ), 83.8 ( $\text{C}=\text{CCH}_3$ ), 14.6 ( $\text{C}_5\text{H}_4\text{CH}_3$ ), 8.0 ( $\text{C}=\text{CCH}_3$ ).  $\text{R} = \text{Pr}^n$  (**3**): IR (THF)  $\nu_{\text{CO}} = 2040$  (m),  $\nu_{\text{CO}} = 1773$  (s)  $\text{cm}^{-1}$  [compare to  $\text{Cp}(\text{NO})(\text{PPh}_3)\text{ReC}=\text{CPh}$ ,  $\nu_{\text{CO}} = 2082$   $\text{cm}^{-1}$ ].