there is no direct correspondence between the observed g values measured for $[Ni(S_2\text{-norbornane})_2]^{1-}$ and for the various spectra for the hydrogenase enzymes.[1]

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.[1] 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.[17]

Acknowledgment. This research was supported by National Institutes of Health Grant GM36308. We thank S. Koch for the X-ray structure determination and for helpful arguments.

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 (Et_4N)-$Li(MeOH)_3(H_2O)[Ni(S_2\text{-}1,2\text{-cyclohexane})_2]$, which is reversibly oxidized to a Ni(III) species in DMSO at $E_{1/2}$ = −0.73 V vs SCE (ΔE_p = 60 mV).

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

Noël Lugan,[1] Colleen Kelley, Michael R. Terry, and Gregory L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

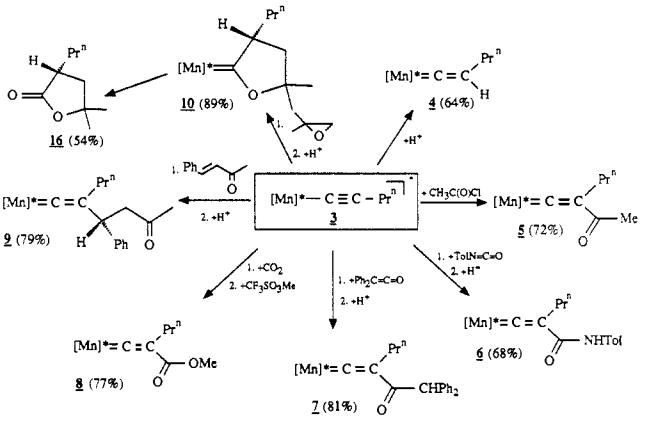
Arnold L. Rheingold

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received November 27, 1989

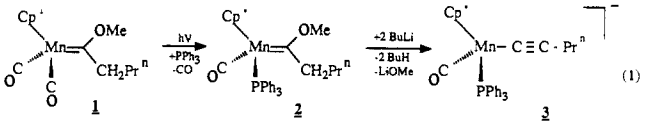
The application of metal–carbene complexes in synthetic organic chemistry is well developed,[2] but one area in need of further exploration is the use of chiral-at-metal carbene complexes in stereospecific syntheses.[3] In an attempt to prepare chiral carbene complexes of the type $Cp'(CO)(PPh_3)Mn{=}C(OMe)CHRR'$ ($Cp' = C_5H_4Me$), 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.[4,5] The starting point for these studies is the carbene

Scheme I[a]



[a] [Mn]* = $Cp'(CO)(PPh_3)Mn$.

complex **2**,[6] which was prepared from complex **1**[7] by photosubstitution of PPh_3 for CO, eq 1. It was anticipated that deprotonation of the β-carbon of the carbene ligand of **2** with BuLi would yield an anionic vinyl complex[8] that upon subsequent addition of R'I would give the desired $Cp'(CO)(PPh_3)Mn{=}C(OMe)CHRR'$. However, a vinyl complex was not formed upon treatment of **2** with BuLi, but instead the anionic acetylide complex **3**[9] was produced, eq 1. Two equivalents of BuLi are necessary



(1)

(1) Present address: Laboratoire de Chimie de Coordination du CNRS, 205 rte de Narbonne, 31077 Toulouse, France.

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

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(4) Illustrated herein are reactions for $[Cp'(CO)(PPh_3)MnC{\equiv}CR]^-$ (R = Pr^n) although similar transformations have been observed for the R = H and R = Me analogues.

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(6) Selected data for the new compounds described herein are as follows. **2**: Anal. C, H. IR (THF): ν_{CO} = 1834 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 340.99 (d, J_{PC} = 23.3 Hz, *C*(OMe)Bu^n). ^{31}P NMR ($CDCl_3$): δ 89.97. **4**: Anal. C, H. IR (THF): ν_{CO} = 1892 (s), $\nu_{C=C}$ = 1633 (w) cm^{-1}. ^{13}C NMR: 364.30 (d, J_{PC} = 30.8 Hz, *C*=CHPr^n), 236.67 (d, J_{PC} = 32.2 Hz, *C*O), 117.89 (s, C=*C*HPr^n). ^{31}P NMR ($CDCl_3$): δ 93.25. **7**: Anal. C, H. IR (THF): ν_{CO} = 1913 (s), ν_{CO} = 1631 (w), $\nu_{C=C}$ = 1545 (s) cm^{-1}. ^{13}C NMR: δ 366.24 (d, J_{PC} = 30.5 Hz, *C*=C(Pr^n)C{O}CHPh$_2$), 235.88 (d, J_{PC} = 30.5 Hz, *C*O), 198.71 (C=C(Pr^n)*C*{O}CHPh$_2$). ^{31}P NMR: δ 86.10. **9**: Anal. C, H. IR (THF): ν_{CO} = 1887 (s), 1713 (w); $\nu_{C=C}$ = 1636 (w) cm^{-1}. ^{13}C NMR: δ 361.39 (d, J_{PC} = 24.3 Hz, *C*=C(Pr^n)CHPhCH$_2$C{O}Me), 237.64 (d, J_{PC} = 33.1 Hz, *C*O), 208.30 (C=C(Pr^n)CHPhCH$_2$*C*{O}Me). ^{31}P NMR: δ 91.85. **10**: Anal. C, H. IR (THF): ν_{CO} = 1832 cm^{-1}. ^{13}C NMR: δ 334.32 (d, J_{PC} = 28.3 Hz, Mn=*C*), 236.90 (d, J_{PC} = 30.5 Hz, *C*O). ^{31}P NMR: δ 88.90.

(7) Prepared from $CpMn(CO)_3$ and 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) $[Cp(CO)(PPh_3)MnC{\equiv}CR]^-$, R = Me: IR (THF) $\nu_{C\equiv C}$ = 2049 (m), ν_{CO} = 1779 (s) cm^{-1}; ^1H NMR (THF-d_8) δ 6.54–6.92 (PPh_3), 4.12, 3.95, 3.87, 3.81 ($C_5H_4CH_3$), 2.64 (s, $C_5H_4CH_3$), 2.62 (s, C≡C*CH*$_3$); ^{13}C NMR (THF-d_8) δ 238.63 (d, J_{PC} = 33.6 Hz, *C*O), 143.9–133.7 (PPh_3), 112.7 (*C*≡CCH$_3$), 97.6, 82.4, 80.8, 80.1, 76.5 (*C*$_5$H$_4$CH$_3$), 83.8 (C≡*C*CH$_3$), 14.6 (C$_5$H$_4$*C*H$_3$), 8.0 (C≡C*C*H$_3$). R = Pr^n (**3**): IR (THF) $\nu_{C\equiv C}$ = 2040 (m), ν_{CO} = 1773 (s) cm^{-1} [compare to $Cp(NO)(PPh_3)ReC{\equiv}CPh$, $\nu_{C\equiv C}$ = 2082 cm^{-1}].

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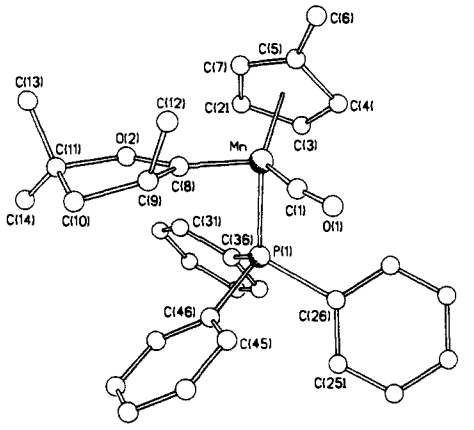
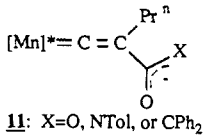


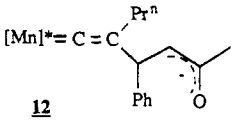
Figure 1. An ORTEP drawing of the methyl analogue of complex **10** prepared from $[Cp'(CO)(PPh_3)MnC{\equiv}CCH_3]^-$.

to drive the complete conversion of **2** into **3** as the addition of a single equivalent gave only an equimolar mixture of these two compounds. Although complex **3** could not be isolated in pure form due to its extreme moisture sensitivity, its nature was inferred from its spectroscopic data[9] and from its detailed reactivity pattern, shown in Scheme I, which illustrates the exceptionally high nucleophilicity of the β-carbon of the acetylide ligand.

All of the products shown in the scheme were isolated as spectroscopically characterized solids,[6] and **9** and the analogue of complex **10** with a CH_3 group replacing the Pr^n group were also characterized by X-ray diffraction studies.[10] Acetylide complex **3** readily undergoes protonation and acylation to give the vinylidene complexes **4** and **5**, and it adds to the heterocumulenes, TolN=C=O, Ph_2C=C=O, and CO_2 to give, after protonation or alkylation, the vinylidene complexes **6**–**8**.[11] These latter complexes likely form via the intermediacy of species **11**. A similar conjugate addition occurs with *trans*-4-phenyl-3-buten-2-one to initially form **12**, which gives the vinylidene complex **9** upon protonation. A significant finding is that complex **9** is



11: X=O, NTol, or CPh_2

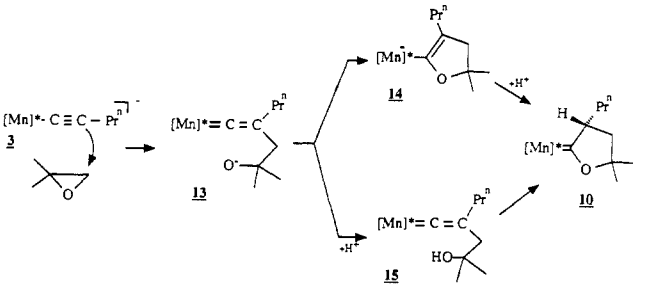


12

produced as a 9:1 mixture of the two possible diastereomers, implying that the chiral Mn center induces a high degree of stereospecificity during the nucleophilic addition step. The crystallographically characterized *RR/SS* stereoisomer of **9** (see supplementary material) is the one expected to form if protonation occurred from the least sterically hindered side of the intermediate vinylidene complex and is presumably the diastereomer that is formed in excess.

One of the most surprising reactions observed for the acetylide complex **3** was its cycloaddition with isobutylene oxide to give the carbene complex **10**. Significantly, NMR data indicate that only a single pair (*RR/SS* or *RS/SR*) of diastereomers of **10** is produced in this reaction, implying that the stereochemical configuration at Mn dictates the configuration adopted at the chiral carbon of the cyclic carbene ligand. The methyl analogue of **10**, prepared from $[Cp'(CO)(PPh_3)MnC{\equiv}CCH_3]^-$, was similarly shown by ^1H NMR to form as a single diastereomeric pair, and this species was crystallographically characterized.[10] The ORTEP drawing shown in Figure 1 indicates that it is the RS/SR pair that has formed, with the CH_3 substituent and the bulky PPh_3 ligand located on opposite sides of the planar metallacycle. As

Scheme II



indicated in Scheme I, oxidation of carbene complex **10** with O_2(g) in dry CH_2Cl_2 releases the free lactone **16**, with was isolated in modest yield (54%). The stereochemical selectivity in the formation of **10** implies that lactone **16** would be produced as a single enantiomer if enantiomerically pure **2** were used in the initial reaction.[12]

The formation of **10** and its methyl analogue likely proceeds via one of the mechanistic paths shown in Scheme II involving initial ring opening of the epoxide to give vinylidene complex **13**. Carbene complex **10** could then form by ring closure to give the vinyl complex **14** followed by protonation at the β-carbon. Alternatively, protonation of **13** could occur prior to ring closure to yield the vinylidene complex **15**, from which **10** would result by addition of the OH bond across the C=C bond of the vinylidene ligand, a characteristic reaction of vinylidene complexes.[5a] In this latter path, the chiral Mn center would dictate the stereochemistry of the final product by sterically controlling the transition state in the ring-closure step. However, if the former path were operative, the stereochemistry of **10** would be dictated by the protonation step, and since protonation should occur from the least hindered face of **14**, the stereochemistry of the product should be *opposite* to that observed. However, the stereoisomer initially formed by this path could epimerize via ring opening to form **15**, which would then give the observed stereoisomer upon the reverse ring closure. Davies has reported a similar epimerization for the iron analogue of **10**.[3d]

The conjugate addition reactions summarized herein for acetylide complex **3** are similar to transformations previously demonstrated for the conjugate bases of metal carbene complexes.[13] The ability of the chiral manganese center in **3** to effectively dictate the chirality of the emerging stereocenter in the organic ligands of **9** and **10** implies that transformations like these may have potential use in stereospecific organic syntheses and could complement the many stereospecific transformations observed by Davies and co-workers for the related acyl complexes $[Cp(CO)(PPh_3)FeC\{O\}CR'R]^-$.[3b-d,14] Current efforts are focused on resolving carbene complex **2** into its separate enantiomers and on extending the addition and cycloaddition reactions reported herein to other organic substrates.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work, NATO for a postdoctoral fellowship to N.L., and the Centre National de la Recherche Scientifique (France) for allowing N.L. to work at PSU.

Supplementary Material Available: Listing of analytical data for compounds **2**, **4**, **5**, **7**, **9**, and **10**, crystallographic data for **9** and the methyl analogue of **10**, atomic positional parameters for **9** and the methyl analogue of **10**, and an ORTEP drawing of **9** (5 pages). Ordering information is given on any current masthead page.

(10) Crystal data: $C_{32}H_{37}O_2MnP$, orthorhombic, $Pna2_1$, a = 28.803 (9) Å, b = 10.018 (4) Å, c = 9.803 (3) Å, V = 2828 (1) Å^3, Z = 4, T = 294 K. Of 2576 data collected, 1863 were unique and observed ($5\sigma F_0$). Considerable disorder was evident in the refined structure, but no chemically sensible model was developed; atoms C_x and C_y were refined as major disorder sites. R = 12.31%, Rw = 13.25%.

(11) See refs 5m,n,q,r for related reactions of metal acetylide complexes with heterocumulenes.

(12) For the preparation of chiral lactones using chiral $Cp(CO)(PPh_3)FeC\{O\}R$ complexes, see ref 3b and see: Davies, S. G.; Middlemiss, D.; Naylor, A.; Wills, M. *Tetrahedron Lett.* **1989**, *30*, 587.

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(14) For a review, see: Davies, S. G.; Dordor-Hedgecock, I. M.; Easton, R. J. C.; Preston, S. C.; Sutton, K. H.; Walker, J. C. *Bull. Soc. Chim. Fr.* **1987**, *4*, 608.