Communication

Syntheses, Fluxional Behavior and Crystal Structures of the *endo* and *exo* η^3-Allyl Monocarbonyl Dithiocarbonate and Dithiocarbamate Molybdenum Complexes: Crystal Structures of *exo*-[Mo(η^3-allyl)(η^2-$S_2COC_2H_5$)(CO)(η^2-dppm)] and *endo*-[Mo(η^3-allyl)(η^2-$S_2CNC_4H_8$)(CO)(η^2-dppe)]

Kuang-Hway Yih[a]* (易光輝), Gene-Hsiang Lee[b] (李錦祥) and Yu Wang[c] (王　瑜)
[a]*Department of Applied Cosmetology, Hung Kuang Institute of Technology, Shalu, Taichung, Taiwan 433, R.O.C.*
[b]*Instrumentation Center, College of Science, National Taiwan University, Taipei, Taiwan, R.O.C.*
[c]*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, R.O.C.*

The novel *endo* and *exo* complexes [Mo(η^3-C_3H_5)(η^2-L_2)(CO)(η^2-dppm)] are accessible by the reactions of the complexes [Mo(η^3-C_3H_5)$(CO)_2$(η^2-L_2)(X)] (L_2, X = S_2COEt, CH_3CN; $S_2CNC_4H_8$; S_2CNEt_2) with dppm. X-ray crystal structures of *exo*-**2** and *endo*-**5** have been employed to elucidate the two orientations.

Fluxionality in the complexes [Mo(η^3-allyl)$(CO)_2(L^1)$-(L^2)X][1] (L^1,L^2: pyrazolylborate, β-diketonate, dithio, X: neutral monodentate ligand; L^1,L^2: diphos, pyridylphosphane, X: halide) is attributed to an intramolecular trigonal twist, in which the rotation of the triangular face formed by the L^1L^2X groups is relative to the face formed by the allyl and the two carbonyl groups. A novel pivoted double switch[2] and a pyridyl-exchange mechanism have been reported when the L^1L^2 ligands were replaced by pyridylphosphane or their oxide ligands. X-ray crystallographic studies of the above-mentioned complexes have so far revealed three different solid-state structures as depicted in Fig. 1 (**A-C**).

The rigid and nonrigid cyclopentadienyl complexes *endo*-, *exo*-*cis*-*syn*-[CpMo(NO)(CO){η^3-CH(Ph)$CHCH_2$}][BF_4][3] and *endo*, *exo*-[(η^5-C_5H_4-COPhe-OMe)Mo(η^3-allyl)$(CO)_2$][4] have become known recently. On the other hand, conformations and fluxional behavior of complexes including Mo(η^3-C_3H_5)(η^2-SS)(CO) moiety have not been very well studied.

Treatment of [Mo(CH_3CN)(η^3-C_3H_5)$(CO)_2$(η^2-S_2COEt)] (**1a**) with dppm in acetonitrile at room temperature yields mixtures of the air-stable and orange-yellow complexes [Mo(η^3-C_3H_5)(η^2-S_2COEt)(CO)(η^2-dppm)] (*endo*, *exo*-**2**) with ca. 88% yield (Scheme I). In the *endo* and *exo* orientations, the open faces of the allyl group point toward the carbonyl group and away from it, respectively. The spectroscopic[5] and analytical data of *endo*, *exo*-**2** are obtained. In the FAB mass spectra, base peaks with the typical Mo isotope distribution are in good agreement with the $[M]^+$ molecular masses of *endo*, *exo*-**2**. The IR spectra of *endo*, *exo*-**2** shows one terminal carbonyl-stretching band at 1801 cm^{-1}. In the ^1H NMR spectrum of *exo*-**2** the methylene protons of the dppm ligand and allyl protons exhibit resonances at δ 2.41, 3.86 and at δ 2.24, 2.55 (H*anti*), 3.78, 4.21 (H*syn*), 4.92 (H*center*), respectively. The corresponding $^{13}C\{^1H\}$ NMR signals are at δ 41.5, and δ 54.5, 58.4, and 68.9. The $^{31}P\{^1H\}$ spectra of

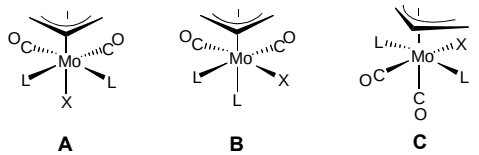
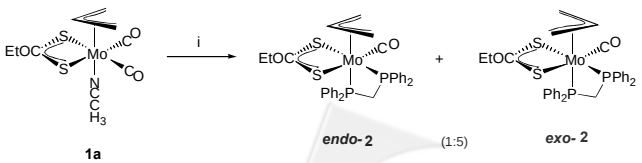


Fig. 1. Three possible structures A, B and C for [Mo(η^3-C_3H_5)$(CO)_2(L^1)(L^2)$X].

Scheme I Reagents and conditions: i, dppm, CH_3CN, r.t., 5 min, 88%

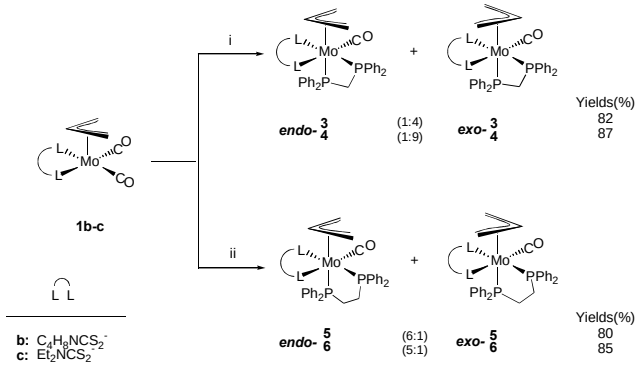


* Corresponding author. Tel: +886-4-26318652 ext. 5308; Fax: +886-4-26321046; E-mail: khyih@sunrise.hkc.edu.tw

endo-, *exo*-**2** show resonances at δ 6.9, 32.8 ($^2J_{P\text{-}P}$ = 52.7) and δ 3.4, 27.4 ($^2J_{P\text{-}P}$ = 63.1) with a 1:5 ratio.

Similar *endo*-**3**,**4** and *exo*-**3**,**4** complexes are prepared by using the 16 electron complexes **1b**,**c** with dppm in refluxing acetonitrile (Scheme II). Ratios of 1:4 and 1:9 of complexes *endo*, *exo*-**3** and *endo*, *exo*-**4** are obtained by integrating from $^{31}P\{^1H\}$ NMR spectra. To investigate the relation between orientations and diphos ligand, we carried out the reactions of **1b-c** with dppe yielding complexes [Mo(η^3-C_3H_5)(η^2-L_2)(CO)(η^2-dppe)][5] (L_2 = $S_2CNC_4H_8$, *endo*, *exo*-**5**; L_2 = S_2CNEt_2, *endo*, *exo*-**6**) with ratios of 6:1 and 5:1, respectively (Scheme II). On the basis of the above-mentioned experiments, we can conclude: (1) the dppm ligand improves the formation of *exo*-products, whereas the dppe ligand improves *endo*-products, and (2) *exo*-complexes show larger $J_{P\text{-}P}$ coupling constants than the *endo*-complexes.

Scheme II Reagents and conditions: i, dppm, CH_3CN, reflux, 1 h; ii, dppe, CH_3CN, reflux, 1 h



The aforementioned conformations of *exo*-**2** and *endo*-**5** have been performed by X-ray diffraction studies at 150 K.[6] ORTEP plots of *exo*-**2** and *endo*-**5** are shown in Figs. 2 and 3, respectively. Clearly, the open face of the allyl group is toward the carbonyl group in *endo*-**5** and away in *exo*-**2**. The two structures confirm unequivalent allyl groups. One of the sulfur atoms of dithioligand is *trans* to the diphos: S(1)-Mo-P(2), 141.77(4)° in *exo*-**2** and S(1)-Mo-P(1), 156.16(2)° in *endo*-**5**, while the other is *trans* to carbonyl: S(2)-Mo-C(1), 167.89(10)° in *exo*-**2** and S(2)-Mo-C(1), 170.65(6)° in *endo*-**5**. The Mo-S and Mo-allyl bond distances in *exo*-**2** and *endo*-**5** are consistent with the values reported for Mo^{II}-S and numerous Mo-allyl systems. The difference between the bond distances and intercarbon angle of allyl group in *exo*-**2** (1.371(7), 1.365(7) Å and 121.5(5)°) and *endo*-**5** (1.399(3), 1.423(3) Å and 116.8(2)°) is not very significant and is in the region of related Mo^{II}-allylic compounds (1.31-1.42 Å, 115-125°).[7]

To test the generality of these reactions, we have studied other Mo-allyl systems. Interestingly, the reactions of [Mo(η^3-C_3H_5)(η^2-L_2)$(CO)_2$(X)] (L_2, X = H_2BPz_2'; pentane-

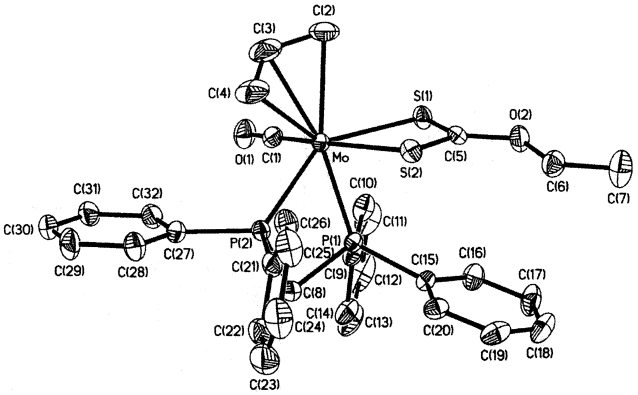


Fig. 2. ORTEP drawing for [Mo(η^3-C_3H_5)(η^2-$S_2COC_2H_5$)(CO)(η^2-dppm)] (*exo*-**2**). Selected bond distances (Å) and angles (°) are as follows: Mo-C(2) 2.357(4), Mo-C(3) 2.328(4), Mo-C(4) 2.341(4), Mo-S(1) 2.5157(6), Mo-S(2) 2.6102(9), C(2)-C(3) 1.371(7), C(3)-C(4) 1.365(4); S(2)-Mo-C(1) 167.89(10), S(1)-Mo-P(2) 141.77(4), C(2)-C(3)-C(4) 121.5(5), P(1)-Mo-P(2) 67.44(3), S(1)-Mo-S(2) 68.53(3).

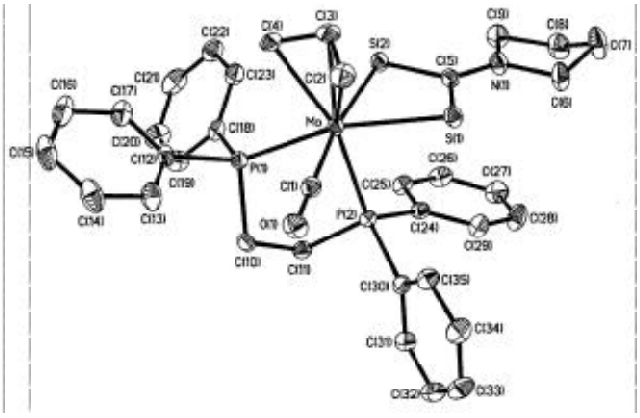


Fig. 3. ORTEP drawing for [Mo(η^3-C_3H_5)(η^2-$S_2CNC_4H_8$)(CO)(η^2-dppe)] (*endo*-**5**). Selected bond distances (Å) and angles (°) are as follows: Mo-C(2) 2.349(2), Mo-C(3) 2.230(2), Mo-C(4) 2.305(2), Mo-S(1) 2.5588(8), Mo-S(2) 2.6248(5), C(2)-C(3) 1.399(3), C(3)-C(4) 1.423(3); S(2)-Mo-C(1) 170.65(6), S(1)-Mo-P(2) 156.160(19), C(2)-C(3)-C(4) 116.8(2), P(1)-Mo-P(2) 78.858(18), S(1)-Mo-S(2) 68.071(17).

2,4-dionate, CH_3CN) with dppm gave $Mo(CO)_2(dppm)_2$ by the replacement of anionic bidentate ligands. This may be due to electronic factors since H_2BPz_2 and pentane-2,4-dionate ligand are weaker donors than dithiocarbamato and dithiocarbonato ligands.

In order to investigate the fluxionality between *endo*, *exo*-**3** and *endo*, *exo*-**5** complexes, the variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in the range of 210 K-333 K. In the range of 210 K-273 K, none of ^1H and $^{31}P\{^1H\}$ NMR spectra changed and the ratio was retained. As depicted in Fig. 4, the variable-temperature $^{31}P\{^1H\}$ NMR spectra show interconversion of *endo*-**5** to *exo*-**5** at 318 K and four doublets of different intensity at 278 K. The line shapes calculated from variable-temperature ^1H NMR spectra[8] of *endo*, *exo*-**3** at 318 K yield values of 15.6 ± 0.2 kcal mol^{-1} for $\Delta G^{\ddagger}$ and 14.8 ± 0.2 kcal mol^{-1} for *endo*, *exo*-**5** at 298 K. The large activation energy of *endo*, *exo*-**3** compared with *endo*, *exo*-**5** is due to the bite angles and that dppm increases the barrier most effectively. Addition of free dppe and $C_4H_8NCS_2^-$ ligand had no effect on these variable-temperature spectra of *endo*, *exo*-**3**,**5** and therefore a rearrangement involving a π-σ-π[9] process or dissociation of the dppe or dithiocarbamato ligand seems unlikely. Noticeably, the original ratios of *endo* and *exo* were retained when the variable-temperature experiments were finished. Compared with other intramolecular trigonal twist rearrangement complexes, the activation energy of *endo*, *exo*-**3**,**5** is larger than those of complexes $[M(\eta^3\text{-}C_3H_5)(CO)_2(diphos)I]$[10] (M = Mo, W; diphos = dppm, dppe) (10.0-11.9 kcal mol^{-1}), $[Mo(CO)(\eta^3\text{-allyl})\{\eta^2\text{-}S_2P(OEt)_2\}(X)]$[11] (X = CH_3CN, 11.6; $C_5H_{10}NH$, 12.6 kcal mol^{-1}) but similar to the allyl rotation complex $[Mo(\eta^5\text{-}C_5H_4\text{-COPhe-OMe})(\eta^3\text{-allyl})(CO)_2]$ (15.0 kcal mol^{-1}).[4] Rotation of the allyl group has been reported in complexes $[CpMo(\eta^3\text{-allyl})(CO)_2]$[12] and $[Pd(\eta^3\text{-allyl})(\eta^2\text{-LL})]$[9] but no example in a $Mo(\eta^3\text{-allyl})(CO)(\eta^2\text{-SS})$ system. The spectral observations on the dynamic species and the data of activation energy[13] of complexes *endo*, *exo*-**3**,**5** reveal that the isomers undergo mutual exchange by the rotation of the metal-allyl bond. The determination of other conformations of complexes with $[Mo(\eta^3\text{-allyl})(CO)(L_1L_1)(L_2L_2)]^+$ type (LL: neutral bidentate ligands) and controlling the regiochemistry of nucleophilic attack on the *endo*, *exo*-complexes are currently under investigation.

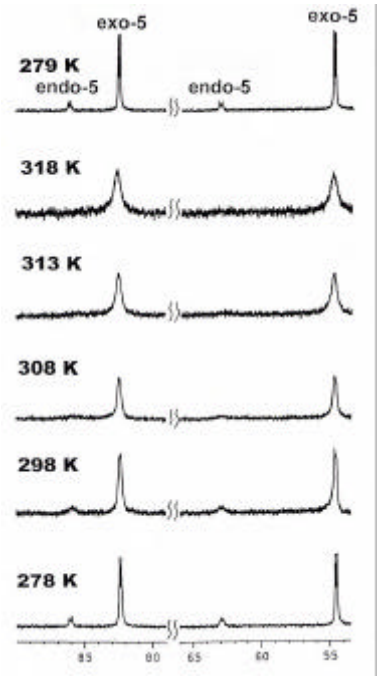


Fig. 4. Variable-temperature $^{31}P\{^1H\}$ NMR observations of the mixture *endo*, *exo*-**5** in $CDCl_3$.

ACKNOWLEDGEMENT

We thank the National Science Council of Taiwan, the Republic of China and Hung Kuang Institute of Technology for support.

Received May 28, 2002.

Key Words

Fluxional behavior; Structures; *endo exo* η^3-allyl stereoisomer; Dithiocarbonate; Dithiocarbamate.

REFERENCES

1. (a) Cotton, F. A.; Frenz, B. A.; Stanislowski, A. G. *Inorg. Chim. Acta* **1973**, *7*, 503. (b) Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074. (c) Brisdon, B. J.; Griffin, G. F. *J. Chem. Soc. Dalton Trans.* **1975**, 1999. (d) Brisdon, B. J.; Woolf, A. A. *J. Chem. Soc. Dalton Trans.* **1978**, 291. (e) Brisdon, B. J.; Dennis, E. A.; Kathleen, E. P. *J. Chem. Soc. Dalton Trans.* **1980**, 1317.
2. Espinet, P.; Hernando, R.; Iturbe, G.; Villafae , F.; Orpen, A. G.; Pascual, I. *Eur. J. Inorg. Chem.* **2000**, 1031.
3. Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161.
4. van Staveren, D. R.; Weyhemüller, T.; Metzler-Nolte, N. *Organometallics* **2000**, *19*, 3730 and references cited therein.
5. *Selected spectroscopic data*: ^1H (300 MHz) and $^{13}C\{^1H\}$ (75

MHz) NMR ($CDCl_3$, relative to $SiMe_4$, multiplicity, assignment, *J* in Hz) $^{31}P\{^1H\}$ (121.5 MHz) NMR (H_3PO_4 external standard). **1a**: IR (KBr, υ_{CO}/cm^{-1}): 1935 (vs), 1860 (vs). ^1H NMR: δ 1.35 (m, 2H, H*anti*), 1.33, (t, 3H, OCH_2CH_3, J_{H-H} = 11.6), 2.05 (br, 3H, CH_3CN), 3.29 (d, 2H, H*syn*, J_{H-H} = 10.8), 4.22 (m, 1H, H*centre*), 4.46 (q, 2H, OCH_2, J_{H-H} = 11.6). $^{13}C\{^1H\}$ NMR: δ 0.9 (s, CH_3CN), 13.1 (s, OCH_2CH_3), 56.4 (br, terminal C of allyl), 67.7 (s, OCH_2), 73.2 (br, centre C of allyl), 116.2 (s, CH_3CN), 227.2 (s, CO). MS (FAB, NBA, *m/z*): 355.9 (M^+). ***Endo***, ***exo*-2**: IR (KBr, υ_{CO}/cm^{-1}): 1801 (vs). MS (FAB, NBA, *m/z*): 672 (M^+), 644 (M^+ - CO). $^{31}P\{^1H\}$ NMR: ***endo*-2**: δ 6.9, 32.8 (d, $^2J_{P-P}$ = 52.7), ***exo*-2**: δ 3.4, 27.4 (d, $^2J_{P-P}$ = 63.1), ^1H NMR: δ 1.10 (t, 3H, OCH_2CH_3, J_{H-H} = 11.7), 2.24, 2.55 (d, 2H, H*anti*, J_{H-H} = 13.3), 2.41, 3.86 (m, 2H, PCH_2), 3.78, 4.21 (m, 2H, H*syn*), 4.00 (m, 2H, OCH_2CH_3), 4.92 (m, 1H, H*centre*). $^{13}C\{^1H\}$ NMR: δ 13.7 (s, CH_3CN), 41.5 (t, PCH_2, J_{P-C} = 20.5), 54.5, 58.4 (s, terminal C of allyl), 66.7 (s, OCH_2), 68.9 (s, centre C of allyl), 222.6 (s, CS_2), 227.1 (s, CO).

***Endo*, *exo*-3**: IR (KBr, υ_{CO}/cm^{-1}): 1781 (vs). MS (FAB, NBA, *m/z*): 685 (M^+ - CO). $^{31}P\{^1H\}$ NMR: ***endo*-3**: δ 4.7, 32.4 (d, $^2J_{P-P}$ = 48.1), ***exo*-3**: δ 1.8, 26.9 (d, $^2J_{P-P}$ = 61.6). $^{13}C\{^1H\}$ NMR: δ 204.0 (d, CS_2, $^3J_{P-C}$ = 3.5), 227.6, 227.7 (s, CO). MS (FAB, NBA, *m/z*): 697 (M^+), 669 (M^+ - CO). ***endo*, *exo*-4**: IR (KBr, υ_{CO}/cm^{-1}): 1806 (vs). MS (FAB, NBA, *m/z*): 671 (M^+ - CO). $^{31}P\{^1H\}$ NMR: ***endo*-4**: δ 4.0, 32.6 (d, $^2J_{P-P}$ = 51.1), ***exo*-4**: δ 0.5, 27.7 (d, $^2J_{P-P}$ = 64.2). ***endo*, *exo*-5**: IR (KBr, υ_{CO}/cm^{-1}): 1791 (vs). MS (FAB, NBA, *m/z*): 711 (M^+), 683 (M^+ - CO). $^{31}P\{^1H\}$ NMR: ***endo*-5**: δ 54.5, 82.3 (d, $^2J_{P-P}$ = 26.1), ***exo*-5**: δ 62.9, 86.0 (d, $^2J_{P-P}$ = 39.1). ***endo*, *exo*-6**: IR (KBr, υ_{CO}/cm^{-1}): 1791(vs). $^{31}P\{^1H\}$ NMR: ***endo*-6**: δ 53.3, 82.7 (d, $^2J_{P-P}$ = 26.1), ***exo*-6**: δ 62.3, 86.6 (d, $^2J_{P-P}$ = 39.3).

6. *Crystal data* for ***exo*-2**: $C_{32}H_{32}MoO_2P_2S_2$, space group $P2_1$, a = 10.2519(2) Å, b = 12.8528(2) Å, c = 11.7698(2) Å, β = 103.0812(9)°, V = 1510.61(5) $Å^3$, Z = 2, D_{calcd} = 1.474 gcm^{-3}, μ = 0.707 mm^{-1}, independent reflections 6668, θ_{range} = 1.78-27.50°. Total number of parameters: 353. *R* = 0.036, R_w = 0.076; GOF = 1.039, Mo Kα radiation; λ = 0.71073 Å; T = 150(1) K; ΔF = 0.946, -0.654e $Å^3$. ***endo*-5**·CH_2Cl_2: $C_{36}H_{39}Cl_2MoNOP_2S_2$, space group $P2_1/n$, a = 11.3200(1) Å, b = 15.8152(2) Å, c = 19.6732(2) Å, β = 90.3932(4)°, V = 3521.97(7) $Å^3$, Z = 4, D_{calcd} = 1.499 gcm^{-3}, μ = 0.764 mm^{-1}, independent reflections 8065, θ_{range} = 1.65-27.50°. Total number of parameters: 407. *R* = 0.029, R_w = 0.074; GOF = 1.118, Mo Kα radiation; λ = 0.71073 Å; T = 150(1) K; ΔF = 0.634, -0.517e $Å^3$. Absorption corrections of *exo*-**2** and *endo*-**5** have been carried out. The two structures were solved by Patterson synthesis and then refined *via* standard least-squares and difference Fourier techniques. Non-hydrogen atoms were refined by using anisotropic thermal parameters.

7. (a) Graham, A. J.; Fenn, R. H. *J. Organomet. Chem.* **1969**, *17*, 405. (b) Cosky, C. A.; Ganis P.; Avatabile, G. *Acta Crystallogr. Sect. B* **1971**, *B27*, 1859. (c) Fenn, R. H.; Graham, A. J. *J. Organomet. Chem.* **1972**, *37*, 137. (d) Cotton, F. A.; Jeremic, M.; Shaver, A. *Inorg. Chim. Acta* **1972**, *6*, 543. (e) Graham, A. J.; Akrigg D.; Sheldrick, B. *Cryst. Struct. Commun.* **1976**, *24*, 173. (f) Cotton, F. A.; Murillo, C. A.; Stults, B. R. *Inorg. Chim. Acta* **1977**, *7*, 503. (g) Brisdon, B. J.; Ewards, D. A.; Paddick, K. E.; Drew, M. G. B. *J. Chem. Soc. Dalton Trans.* **1980**, 1317. (h) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227. (i) Lush, S. F.; Wang, S. H.; Lee, G. H.; Peng, S. M.; Wang, S. L.; Liu, R. S. *Organometallics* **1990**, *9*, 1862.
8. Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie,* 3rd ed.; Georg Thieme Verlag: Stuttgart, New York, 1987.
9. (a) Chowdhury, S. K.; Nandi, M.; Joshi, V. S.; Sarkar, A. *Organometallics* **1997**, *16*, 1806 and references cited therein. (b) Kollmar, M.; Goldfuss, B.; Reggelin, M.; Rominger, F.; Helmchen, G. *Chem. Eur. J.* **2001**, *7*, 4913.
10. Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.
11. Yih, K. H.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1999**, *588*, 125.
12. (a) King, R. B. *Inorg. Chem.* **1966**, *5*, 2242. (b) Davison, A.; Rode, W. C. *Inorg. Chem.* **1967**, *6*, 2124.
13. Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.