yield,[7] along with 21% $Cr(CO)_6$.[19] Carbene complex **3** cannot be observed by high pressure liquid chromatography after 20 h under these reaction conditions. Increasing the concentration of **3** and/or decreasing the H_2 pressure leads to severely decreased yields of THF. A 23% yield of THF is obtained at 3.4 atm of H_2, employing a solution 1.67 times as concentrated in **3**, compared to the data above. Under these conditions, some $\overline{O(CH_2)_3C}=\overline{C(CH_2)_3O}$ (the product of the second-order thermal decomposition of **3**[11]) was observed. This indicates that the reduced yields of THF obtained at lower H_2 pressure and higher concentrations are due to competition between the hydrogenation and thermal decomposition of **3**.

2,3-Dihydrofuran is known to be a product of the base-catalyzed decomposition of **3**,[11] and the question arises as to whether the THF observed in the reduction of **3** by H_2 could be formed by the reduction of 2,3-dihydrofuran generated from the carbene complex. To test this experimentally, **3** was reacted with 69 atm of D_2 (Matheson Gas Products, 99.5%) at 170 °C in decalin for 48 h. The ratio of α to β proton resonances in the THF formed in the reaction was 1:2, demonstrating that the product was α,α-dideuteriotetrahydrofuran. The absence of α,β-dideuteriotetrahydrofuran clearly indicates that 2,3-dihydrofuran is not a precursor to THF.

Substitution at the α-carbon atom, the position most easily modified via the conjugate anion of chromium carbene complexes,[14] does not seem to adversely affect the yield of the cleavage reaction. In fact, **4**[17,20] is reduced in decalin under much lower pressures (4.4 atm of H_2, 240 °C) than required for reduction of **3**. Reaction of **4** with molecular hydrogen yields 3,3-dimethyltetrahydrofuran (72%)[7] along with $Cr(CO)_6$[19] (12%). No unreacted **4** is observed by high pressure liquid chromatography. The required temperature increase for reduction of **4** relative to **3** parallels their relative thermal stabilities.[10,20]

Our studies have shown that group 6 metal carbene complexes are reduced by molecular hydrogen to give the corresponding organic products, and that this reaction can serve as a model for the chain termination step in the metal catalyzed reduction of CO by H_2. We are currently exploring the reaction of these model complexes with mixtures of H_2 and CO to determine whether chain extension as well as chain termination can occur under these conditions.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged.

References and Notes

(1) This process has been reviewed (a) P. H. Emmett, Ed., "Catalysis", Vol. 4, Reinhold, New York, N.Y., 1956; (b) H. H. Storch, N. Golumbic, and R. B. Anderson, "The Fischer-Tropsch and Related Synthesis", Wiley, New York, N.Y., 1951.
(2) I. Howard-Smith and G. J. Werner, "Coal Conversion Technology 1976", Chemical Process Technology Review No. 66, Noyes Data Corporation, Park Ridge, N.J., 1976.
(3) M. A. Vannice, *J. Catal.*, **37**, 449, 462 (1975).
(4) C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976).
(5) G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **15**, 136 (1976).
(6) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973); (b) C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *ibid.*, submitted for publication.
(7) Reported yields were determined by gas chromatography employing an internal standard, and the products were identified by retention times and either mass spectrometry or ^{1}H NMR.
(8) The solvent is believed to participate when diphenylmethane is produced on thermolysis of **1**.[6b,9]
(9) T. J. Burkhardt, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1974.
(10) R. L. Anderson, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1974.
(11) C. P. Casey and R. L. Anderson, *J. Chem. Soc., Chem. Commun.*, 895 (1975).
(12) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).
(13) C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, **102**, 175 (1975).
(14) C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Am. Chem. Soc.*, **94**, 8947 (1972).
(15) C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, in press.
(16) C. P. Casey, S. H. Bertz, and T. J. Burkhardt, *Tetrahedron Lett.*, 1421 (1973).
(17) C. P. Casey in "New Applications of Organometallic Reagents in Organic Synthesis", J. Organomet. Chem. Library 1, D. Seyferth, Ed., Elsevier, Amsterdam, 1976.
(18) C. P. Casey and R. L. Anderson, *J. Organomet. Chem.*, **73**, C28 (1974).
(19) Products were identified by high pressure liquid chromatography using coinjection techniques, and yields were obtained using an internal standard.
(20) C. P. Casey, R. L. Anderson, and D. A. Pepitone, unpublished results.

Charles P. Casey,* Stephen M. Neumann
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received November 8, 1976

Hexakis(neopentoxy)dimolybdenum. Preparation, Characterization, and Reactions with Lewis Bases and Carbon Dioxide

Sir:

We report the synthesis and characterization of $Mo_2(OCH_2CMe_3)_6$, together with some of its reactions. This work provides the first structural characterization of a dinuclear alkoxide in which transition metal atoms are directly bonded and unsupported by bridging alkoxy ligands,[1] and the chemistry of $Mo_2(OCH_2CMe_3)_6$ shows that it is coordinatively unsaturated. It reversibly binds donor molecules such as amines and phosphines to give adducts of the type $Mo_2(OCH_2CMe_3)_6 \cdot L_2$. In alkane solvents $Mo_2(OCH_2CMe_3)_6$ is unstable and oligomerizes to an insoluble form of the alkoxide $[Mo(OCH_2CMe_3)_3]_n$. In addition, $Mo_2(OCH_2CMe_3)_6$ reacts reversibly with CO_2 in hydrocarbon solvents to give $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$.

Hydrocarbon solutions of $Mo_2(NMe_2)_6$[2] react rapidly with neopentanol (≥6 equiv) at room temperature to give $Mo_2(OCH_2CMe_3)_6(HNMe_2)_2$, which is a red crystalline compound, readily isolated in the above reaction by merely stripping the solvent.[3] Upon heating to 50 °C in vacuo dimethylamine is evolved and at 100-120 °C, 10^{-3} Torr, yellow-green crystals of $Mo_2(OCH_2CMe_3)_6$ sublime.

A strong parent ion $Mo_2(OCH_2CMe_3)_6{}^+$ and many other Mo_2-containing ions were observed in the mass spectrometer. The virtual absence of mononuclear ions was quite striking.

^{1}H[4] and ^{13}C[5] NMR spectra at room temperature were as expected for the presence of only one kind of alkoxy group. On lowering the temperature the signals remained sharp to ca. −30 °C in toluene-d_8, but at lower temperatures all resonances broadened until at −80 °C in both the ^{1}H and ^{13}C spectra the methylene signals were lost into the baseline. We tentatively

Table I. Relevant Interatomic Distances (Å) and Angles (deg)[a-c]

Atoms	Distance	Atoms	Distance
Mo-Mo′	2.222 (2)	Mo-O(2)	1.867 (6)
Mo-O(1)	1.905 (6)	Mo-O(3)	1.855 (6)

Atoms	Angle	Atoms	Angle
Mo′-Mo-O(1)	98.3 (2)	O(2)-Mo-O(3)	114.0 (3)
Mo′-Mo-O(2)	105.5 (2)	Mo-O(1)-C(1)	114.5 (7)
Mo′-Mo-O(3)	105.4 (2)	Mo-O(2)-C(6)	135.1 (6)
O(1)-Mo-O(2)	115.9 (3)	Mo-O(3)-C(11)	134.2 (6)
O(1)-Mo-O(3)	115.2 (3)		

[a] The numbers in parentheses are the estimated standard deviation in the least significant digits. [b] Atoms are labeled as in Figure 1. [c] Primed atoms are related by a crystallographic inversion center to the corresponding unprimed atoms.

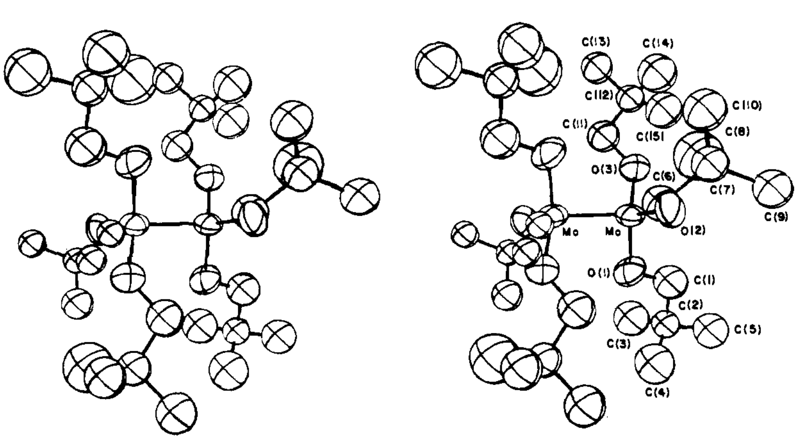


Figure 1. An ORTEP stereoscopic view of the $Mo_2(OCH_2CMe_3)_6$ molecule showing 50% probability ellipsoids and atomic numbering scheme.

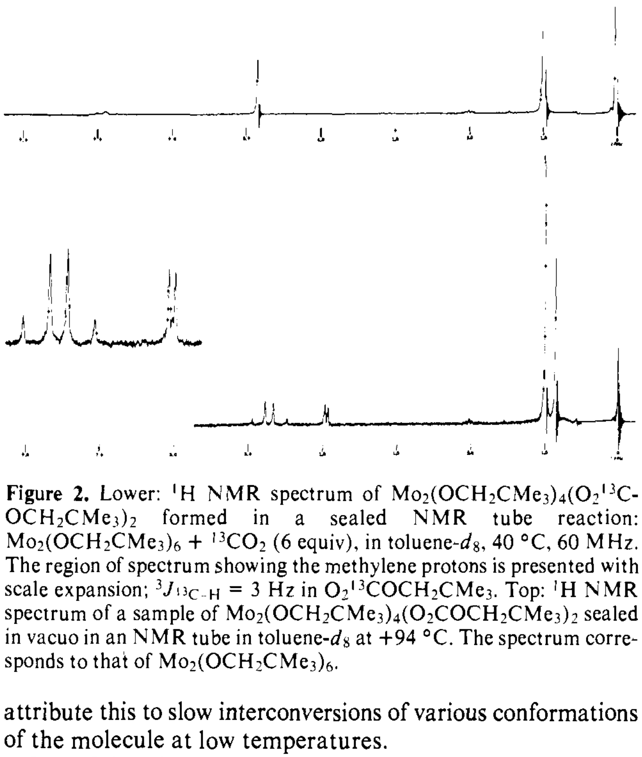


Figure 2. Lower: ^{1}H NMR spectrum of $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ formed in a sealed NMR tube reaction: $Mo_2(OCH_2CMe_3)_6$ + $^{13}CO_2$ (6 equiv), in toluene-d_8, 40 °C, 60 MHz. The region of spectrum showing the methylene protons is presented with scale expansion; $^3J_{^{13}C-H}$ = 3 Hz in $O_2{}^{13}COCH_2CMe_3$. Top: ^{1}H NMR spectrum of a sample of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$ sealed in vacuo in an NMR tube in toluene-d_8 at +94 °C. The spectrum corresponds to that of $Mo_2(OCH_2CMe_3)_6$.

attribute this to slow interconversions of various conformations of the molecule at low temperatures.

$Mo_2(OCH_2CMe_3)_6$ reacts rapidly in hydrocarbon solutions with NH_3, $MeNH_2$, Me_2NH, and PMe_2Ph to give adducts $Mo_2(OCH_2CMe_3)_6{\cdot}L_2$.[6] Upon heating in vacuo, the Lewis bases are eliminated and $Mo_2(OCH_2CMe_3)_6$ is regenerated. The structure of these adducts is not yet known.

Although $Mo_2(OCH_2CMe_3)_6$ appears indefinitely stable in the crystalline state when sealed in ampoules in vacuo, in hydrocarbon solvents an irreversible reaction occurs leading to the precipitation of a brick-red, insoluble, and nonvolatile powder which, on the basis of analytical data,[7] we formulate as a polymeric form of the alkoxide, $[Mo(OCH_2CMe_3)_3]_n$.

These observations contrast with the behavior of the related dinuclear alkyls Mo_2R_6[8] (R = CH_2CMe_3 and CH_2SiMe_3) and dialkylamides $Mo_2(NR_2)_6$[2] (R = Me, Et) which show no affinity toward donor molecules and have no tendency toward oligomerization.

We proceeded toward a full structural characterization of this interesting, coordinatively unsaturated dinuclear alkoxide. Crystals[9] were obtained from pentane at −78 °C under rapid growth conditions (<1 h) to avoid contamination with $[Mo(OCH_2CMe_3)_3]_n$. Figure 1 shows a view of the molecule and Table I lists some of the important structural parameters. $Mo_2(OCH_2CMe_3)_6$ is structurally similar to the compounds $Mo_2(NMe_2)_6$[2] and $Mo_2(CH_2SiMe_3)_6$:[8] The central Mo_2X_6 moiety (X = C, N, O) has virtual D_{3d} symmetry and the Mo–Mo interatomic distances are in the range 2.167–2.222 Å. Evidently, there is a class of compounds of general formula M_2L_6, where L = R (alkyl), NR_2, and OR, in which the metals (M = Mo, W[8-11]) are directly bonded and unsupported by bridging ligands.

The steric congestion about molybdenum in the Mo_2L_6 series is clearly less for L = OCH_2CMe_3 than for NMe_2[2] and CH_2SiMe_3.[8] It is possible to fit at least five OCH_2CMe_3 ligands about a second-row transition metal.[12] The structure of $Mo_2(OCH_2CMe_3)_6$ is particularly interesting since the neopentoxy group provides the point of departure from the $L_3Mo{\equiv}MoL_3$ structure to a $[Mo(OR)_3]_n$ structure.[13]

$Mo_2(OCH_2CMe_3)_6$ reacts in hydrocarbon solvents with carbon dioxide to give $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$. This contrasts with the reactions of related dialkylamides, e.g.,[14,15] $W_2(NMe_2)_6 + CO_2 \rightarrow W_2(O_2CNMe_2)_6$. The reaction between $Mo_2(OCH_2CMe_3)_6$ and CO_2 is completely reversible: at 35 °C the equilibrium position favors the alkylcarbonate. This is quite evident for the ^{1}H NMR spectra shown in Figure 2. The methylene protons $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$ are seen to be diastereotopic at +35 °C: A plane of symmetry, either real or apparent on the NMR time scale, cannot contain the two molybdenum atoms and the four oxygen atoms of the $Mo_2(OR)_4$ moiety. The structure of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$ may be related to those found[14] for $W_2(O_2CNMe_2)_6$ and $W_2Me_2(O_2CNEt_2)_4$ which contain two bridging O_2CNR_2 ligands.

Acknowledgment. We thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) at Princeton University and the National Science Foundation (Grant No. GP 33142X) at Texas A&M University for support of this work.

References and Notes

(1) For reviews of metal alkoxide chemistry, see (a) D. C. Bradley, *Prog. Inorg. Chem.*, **2**, 333 (1960); (b) *Adv. Inorg. Chem. Radiochem.*, **15**, 159 (1972); (c) D. C. Bradley and K. J. Fisher, *MTP Int. Rev. Sci.*, **5**, Part I, 65 (1972).

(2) (a) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976); (b) M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, and L. Shive, *J. Chem. Soc., Chem. Commun.*, 480 (1974); (c) M. H. Chisholm and W. W. Reichert, *J. Am. Chem. Soc.*, **96**, 1249 (1974).

(3) The molybdenum compounds described here are all readily hydrolyzed in moist air. Standard precautions and manipulations for the handling of air-sensitive compounds were used. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(4) ^{1}H NMR data, 40 °C, toluene-d_8, 60 MHz: δ(CH$_2$) 4.93, δ(CH$_3$) 1.08. δ parts per million relative to Me$_4$Si.

(5) ^{13}C NMR data, 38 °C, toluene-d_8, Varian XL 100 FT spectrometer: δ(O*C*H$_2$) 86.7; δ(*C*Me$_3$) 34.5, δ(C(*C*H$_3$)$_3$) 26.7; δ in parts per million relative to Me$_4$Si.

(6) NMR data for $Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$ recorded in toluene-d_8 at +38 °C; δ(C*H*$_2$) 4.40, δ(N(C*H*$_3$)$_2$) 2.40, δ(C(C*H*$_3$)$_3$) 1.05, δ(O*C*H$_2$) 82.9, δ(OCH$_2$*C*Me$_3$) 34.3, δ(OCH$_2$C(*C*H$_3$)$_3$) 27.3; δ(N(*C*H$_3$)$_2$) 40.3. δ in parts per million downfield from Me$_4$Si.

(7) Calcd. for $[Mo(OCH_2CMe_3)_3]_n$: C, 50.41; H, 9.33. Found: C, 50.33; H, 9.14. Cf. analysis of yellow-green crystals of $Mo_2(OCH_2CMe_3)_6$. Found: C, 50.08; H, 9.18.

(8) F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971); G. Wilkinson and W. Mowat, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).

(9) Crystal data for $Mo_2(OCH_2CMe_3)_6$: space group, $P21/n$; $a = 18.160\ (10)$, $b = 11.051\ (7)$, $c = 9.956\ (6)$ Å; $\beta = 104.30\ (4)^0$; $V = 1936\ (2)$ Å^3; $Z = 2$; Mo radiation; 1588 reflections having $I > 3\sigma(I)$ and $2\theta \leq 45^0$. Refined anisotopically to $R_1 = 0.071$ and $R_2 = 0.088$.

(10) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4477 (1976).

(11) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97**, 5625 (1975).

(12) $Nb(OCH_2CMe_3)_5$ is monomeric in benzene, $Zr(OCH_2CMe_3)_4$ is dimeric in benzene. See ref 1 and references therein. We have recently prepared $Mo(OCH_2CMe_3)_4$ and find this to be dimeric in solution. M. H. Chisholm and W. W. Reichert, unpublished work.

(13) The reaction $Mo_2(NMe)_6 + 6ROH \rightarrow Mo_2(OR)_6$ was previously noted for R = *t*-Bu and SiMe$_3$ (ref 2c); for less bulky groups, e.g.; R = Et, Me, dinuclear compounds $Mo_2(OR)_6$ are not isolated. Results to be submitted for publication.

(14) M. H. Chisholm, F. A. Cotton, M. W. Extine, B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4683 (1976).

(15) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, submitted for publication.

Malcolm H. Chisholm,* William W. Reichert
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

F. Albert Cotton,* Carlos A. Murillo
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received September 17, 1976

Chirality Retention in Twist Rearrangements of Pseudooctahedral Molybdenum and Tungsten Complexes

Sir:

We wish to present new evidence for a type of stereochemically nonrigid behavior which is capable of maintaining chirality while allowing interconversion of certain isomers. The rearrangement appears to involve a trigonal twist about a specific axis of a pseudooctahedral complex. This mechanism and the unique structural features proposed for (η^3-C$_3$H$_5$)Mo(CO)$_2$(diphos)Cl and similar complexes are based on recent crystallographic and NMR results.

Low temperature ^{13}C NMR spectra of (η^3-C$_3$H$_5$)-Mo(CO)$_2$(diphos)Cl show that the two carbonyl ligands are nonequivalent. This contrasts with previous structural studies of analogous diamine and diether chelates,[1-6] which imply that the carbonyls should occupy equivalent positions in a pseudooctahedron. In the diamine and diether structures the bidentate ligand and the two carbonyls lie in a horizontal plane, whereas the allyl group and the remaining ligand lie in trans positions above and below the plane, respectively, as in configuration I. Either structure II or III would be consistent with most aspects of the low temperature NMR spectra, but the nature of the inequivalence was revealed straightforwardly by a three-dimensional x-ray crystallographic analysis. The molecular structure[7,8] is as shown in Figure 1. This establishes that the molecule can be appropriately described as pseudooctahedral.[9] An equatorial plane[10] can be defined to include the two carbonyls, the halogen, and one phosphorus atom of the chelate. The η^3-C$_3$H$_5$ ligand and the other phosphorus of the chelate ligand lie on opposite sides of this plane. Thus the complex has no plane of symmetry, which is consistent with the NMR results, and can be schematically represented by configuration III.

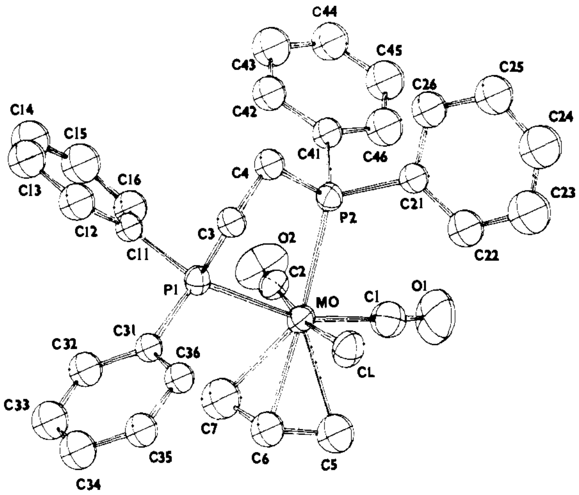
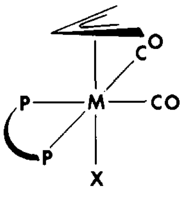
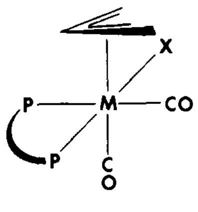


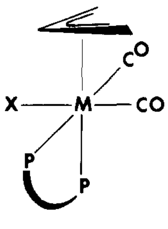
Figure 1. A perspective view of (η^3-C$_3$H$_5$)Mo(CO)$_2$(diphos)Cl. Hydrogen atoms are not shown.



I



II



III

We have found that complexes of the general formula η^3-C$_3$H$_5$M(CO)$_2$(L-L)X where M = Mo or W; L-L = the bidentate phosphines[11,12] diphos, dppm, dppe, or arphos; and X = Cl or I exhibit dynamic ^{1}H, ^{13}C, and ^{31}P NMR spectra indicative of intramolecular rearrangement barriers on the order of 12 kcal/mol.

The room temperature ^{31}P-decoupled proton NMR spectra of the iodide complexes containing diphos, dppe, or dppm exhibit three sets of resonances for the allyl moiety, typical of the AA′BB′X pattern of symmetrical η^3-allyls. At low temperatures, however, nonequivalence of the two ends of the allyl is indicated by an ABCDX pattern.[13] In the diphos complex, the diphos methylene protons appear as an ABCD pattern at −100 °C and an AA′BB′ pattern at 30 °C. The methylene protons of the dppm, however, remain nonequivalent and exhibit an AB pattern throughout the temperature range in which the allyl resonances average.[13]

Except in the arphos derivative, the ^{13}C spectra indicate equivalence of the terminal carbon nuclei of the allyl moiety and the carbonyls. The averaged spectra of the diphos complexes exhibit an apparent triplet for the methylene carbons. At low temperatures, the terminal carbons of the allyl, the carbonyl carbons, and the methylene carbons of the diphos ligand are nonequivalent.

The ^{31}P spectra of the complexes consist of a single resonance at room temperature and two (or four depending upon the resolution of ^{31}P–^{31}P coupling) lines of equal intensity at low temperature.

The infrared spectra are characteristic of cis-carbonyls; i.e., two carbonyl absorptions of approximately equal intensity are observed. Thus, the spectral data indicate that the solution structure is the same as that found in the crystal. A rear-