Optical yields of this magnitude for carbon–carbon bond forming reactions at normal temperatures (70–80 °C) in a catalytic process are among the highest seen and suggest this approach as an exciting solution to asymmetric induction in carbon–carbon bond forming reactions. The higher optical yields in the case of allylic acetate **5** may arise in part due to the fact that the intermediate π-allylpalladium complexes with chiral phosphines are diastereomeric. Most strikingly, the present observations demand a racemization of **5** or an interconversion of diastereomers of the intermediate π-allyl complexes accompanying the conversion of **5** to **7** and thus may be contrasted to our earlier work.[3] While several rationales can be envisioned and detailed discussion will be reserved for a future publication, it appears that the slower rates of alkylation due to the presence of excess phosphine relative to palladium allows a palladium catalyzed acetate ion induced racemization of the starting allylic acetate to compete with alkylation.

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References and Notes

(1) (a) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975); (b) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Adv. Chem. Ser.*, **No. 132**, 274 (1974); (c) T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975); (d) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972); (e) N. Takaishi, H. Imai, C. A. Bertelo, and J. K. Stille, *ibid.*, **98**, 5400 (1976).

(2) For reviews see (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice Hall, Englewood Cliffs, N.J., 1971; (b) B. Bogdanovic, *Angew. Chem., Int. Ed. Engl.*, **12**, 954 (1973); (c) also see G. Consiglio, *Helv. Chim. Acta*, **59**, 124 (1976). (d) For a stoichiometric case see B. M. Trost and T. J. Dietsche, *J. Am. Chem. Soc.*, **95**, 8200 (1973).

(3) B. M. Trost and T. R. Verhoeven, *J. Org. Chem.*, **41**, 3215 (1976); *J. Am. Chem. Soc.*, **98**, 630 (1976).

(4) M. E. Kuehne, J. E. Saavedra, and P. J. Reider, Abstracts of the First Chemical Congress of the North American Continent, Mexico City, Mexico, 1975, Orga 126.

(5) B. M. Trost, H. C. Arndt, P. E. Strege, and T. R. Verhoeven, *Tetrahedron Lett.*, 3477 (1976).

(6) O. Ceder and B. Hansson, *Acta Chem. Scand.*, **24**, 2693 (1970).

(7) J. S. Stanton, Ph.D. Thesis, University of Wisconsin, 1975. We are most grateful to Dr. J. Timko for generous samples of optically active hydroxy ester.

(8) B. M. Trost and L. Weber, *J. Org. Chem.*, **40**, 3617 (1975); J. McMurry and G. B. Wong, *Synth. Commun.*, **2**, 389 (1972).

(9) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, **93**, 5913 (1971).

(10) For this catalyst, the procedure of Coulson (D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972)) was employed except that the triphenylphosphine was replaced by 4 mol of (+) DIOP. The yellow solid was utilized directly without further purification. The lower catalytic activity of this catalyst precluded its broader application.

(11) J. D. Morrison, *Pet. Res. Found. Annu. Rep.*, **18**, 165 (1973); J. D. Morrison, W. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25**, 81 (1976); J. D. Morrison, W. F. Masler, and S. Hathaway, "Catalysis in Organic Synthesis—1976", Academic Press, New York, N.Y., 1976, pp 203–233.

Barry M. Trost,* Paul E. Strege
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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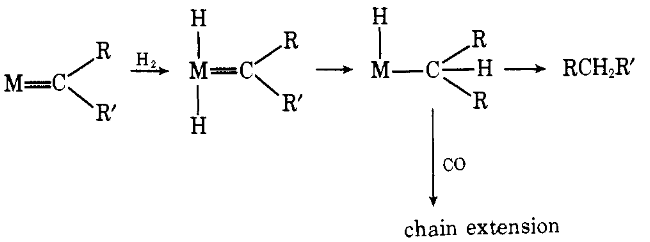
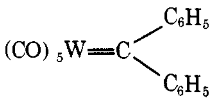
Reaction of Molecular Hydrogen with Transition Metal Carbene Complexes: Reductive Cleavage of the Carbene Ligand

Sir:

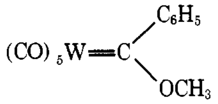
The current shortage of petroleum has focused renewed attention on alternative methods of producing organic fuels. The reduction of coal-derived carbon monoxide/hydrogen mixtures by heterogeneous transition metal catalysts in the Fischer–Tropsch process is one such alternative.[1-3] However, little is known about the mechanism of these reductions. We have previously reported the synthesis and properties of several transition metal formyl complexes,[4] which may well serve as models for the first intermediate in the reduction of CO by H_2. Our continued interest in this area has led us to study the reaction of molecular hydrogen with metal carbene complexes, a process which may be related to the chain-termination step of the Fischer–Tropsch synthesis[5] (Scheme I). Here we report that the tungsten and chromium carbene complexes **1–4** react with molecular hydrogen to give organic products derived from reductive cleavage of the carbene ligand.

Scheme I

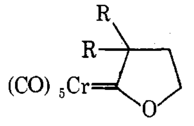




1



2



3, R = H
4, R = CH_3

The diphenylcarbene complex, **1**,[6] which does not possess stabilizing heteroatom substituents bonded to the carbene carbon, was chosen as one of the best available models for the alkyl–hydrido type of metal carbene complexes postulated as intermediates in the Fischer-Tropsch reaction. When **1** is dissolved in decalin and reacted at 100 °C for 20 h with 69 atm of H_2, a 41% yield of diphenylmethane is obtained,[7] along with small amounts of tetraphenylethylene and tetraphenylethane. $W(CO)_6$ (58% by IR analysis) is the only identified tungsten containing product, and TLC analysis indicates that **1** is totally consumed during the reaction. Hydrogenation of **1** in benzene-d_6 gives Ph_2CH_2 (100% d_0), which indicates that solvent does not participate in product formation.[8] The temperatures employed in the reduction reactions of all the carbene complexes (**1–4**) are generally in excess of those required for thermal decomposition and for ^{13}CO exchange.[9-11] A prior dissociation of CO may well be required for these reductions.

Phenylmethoxycarbene complex **2**,[12] reacts with H_2 to give significantly higher yields of organic product than its nonheteroatom stabilized counterpart, **1**. Thus, a solution of **2** in decalin reacts with 1.8 atm of H_2 at 140 °C for 5 h to give benzyl methyl ether (92%), toluene (3%), bibenzyl (1%), *trans*-stilbene (1%), and *E*- and *Z*-α,α'-dimethoxystilbene (3%).[7] The higher temperature required for this reaction parallels the higher temperatures required for the thermal decomposition and the ^{13}CO exchange of **2** compared with **1**.

The reaction of H_2 with **3** and **4** was studied primarily to determine if the carbene ligand could be cleaved reductively from these cyclic complexes in a synthetically useful manner. Since **3** and related compounds have been shown to be easily elaborated[13-15] and useful in organic synthesis,[16,17] a reductive cleavage of the carbene ligand could be a synthetically important procedure. We have found that cleavage does occur in good yields. For example, reaction of **3**[18] with 69 atm of H_2 in decalin at 170 °C gives tetrahydrofuran (THF) in 95%

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.

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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 ^1H 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

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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.

^1H[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 ^1H 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.