chemistry, where (1-electron donor) phenyl rings bridge between coppers. Finally, the results reported here call attention to the possibility that some of the numerous phosphino gold clusters,[16-17] many of which are synthesized by using BH_4^-, contain undiscovered hydride ligands.

Supplementary Material Available: Atomic positional and thermal parameters for the two copper hydrides (4 pages). Ordering information is given on any current masthead page.

(15) Khan, S. I.; Edwards, P. G.; Yuan, H. S. H.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1682.
(16) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.
(17) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237.

Formation of Stable Tungsten Alkene Carbyne Complexes by Carbonyl Substitution Reactions

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Received July 2, 1985

Reactions of alkenes and alkynes with metal complexes containing unsaturated metal–carbon bonds have been the subject of continued interest because of their involvement in olefin[1] and acetylene[2] metathesis, as well as polymerization[3] reactions. *trans*-Halotetracarbonyltungsten carbyne complexes have been shown to induce polymerization of both certain alkenes[4] and alkynes.[5] We have recently[6] developed simple synthetic routes to substituted carbyne complexes $X(CO)_2(L)_2M\equiv CR$ (X = halide; L = nitrogen donor ligand; M = Cr, Mo, W) and have begun to investigate reactions of tungsten systems with unsaturated organic molecules. Here we wish to report ligand substitution reactions that provide easy access to a new class of tungsten carbyne complexes containing alkene ligands.[7]

Reaction of the bis(pyridine)-substituted carbyne complexes $Cl(CO)_2(py)_2W\equiv CR$, **1** and **2** (**1**, R = C_6H_5; **2**, R = CH_3), with excess (10 equiv) tetraethylammonium chloride in dichloromethane affords the anionic carbyne complexes $NEt_4[Cl_2(py)(CO)_2W\equiv$

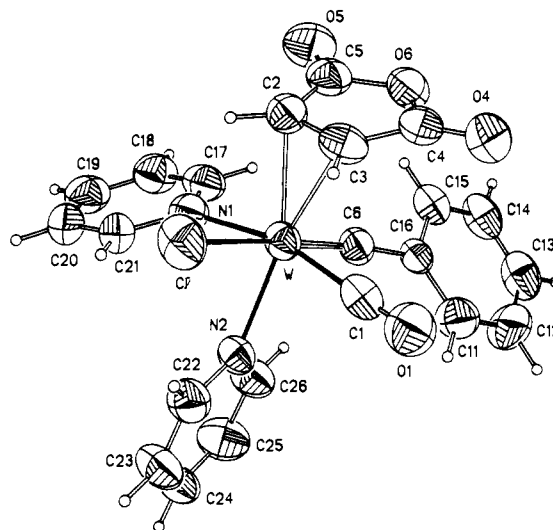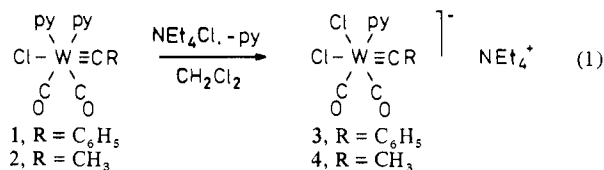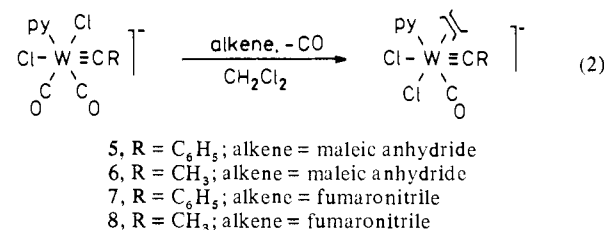(1) (a) Grubbs, R. H. In "Comprehensive Organometallic Chemistry", Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 499–551.
(2) (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554–1562. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563–1573.
(3) (a) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331–2333. (b) Ivin K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604–606.
(4) Fischer, E. O.; Wagner, W. R. *J. Organomet. Chem.* **1976**, *116*, C21–C22.
(5) Katz, T. J.; Ho, T. H.; Shih, N.-Y.; Ying, Y.-C.; Stuart, Van I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2659–2668.
(6) (a) Mayr, A.; Schaefer, K. C.; Huang, E. Y. *J. Am. Chem. Soc.* **1984**, *106*, 1517–1518. (b) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608–610.
(7) The only previous example of this type of complex is (CF_3SO_3)-$(PMe_3)_3(C_2H_4)W(CH)$; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476–484.

Figure 1. Molecular structure of $Cl(CO)(maleic\ anhydride)(py)_2W\equiv$ CPh (**9**). 50% thermal ellipsoids. W–C(6), 1.801 (6); W–N(1), 2.233 (5); W–N(2), 2.253 (4); W–Cl, 2.538 (1); W–C(1); 2.033 (6); W–C(2), 2.215 (6); W–C(3), 2.272 (6); C(2)–C(3), 1.408 (8) Å. Cl–W–C(6), 171.2 (2)°; N(1)–W–C(1), 165.4 (2)°; [M = midpoint of C(2)–C(3)] M–W–N(2), 170.8 (2)°; M–W–C(6), 96.4 (2)°; M–W–C(1), 91.4 (2)°; M–W–N(1), 102.1 (2)°; M–W–Cl, 83.2 (1)°.

CR], **3** and **4** (**3**, R = C_6H_5; **4**, R = CH_3) (eq 1).[8] These products are only stable in the presence of excess chloride.[9]

$$\begin{array}{ccc} \underset{Cl-\underset{\underset{O}{C}}{\overset{py}{\underset{\diagup}{W}}}\underset{\underset{O}{C}}{\equiv}CR}{} & \xrightarrow[CH_2Cl_2]{NEt_4Cl,\ -py} & \left[\underset{Cl-\underset{\underset{O}{C}}{\overset{Cl}{\underset{\diagup}{W}}}\underset{\underset{O}{C}}{\equiv}CR}{\overset{py}{}}\right]^- NEt_4^+ \end{array} \quad (1)$$

1, R = C_6H_5
2, R = CH_3 3, R = C_6H_5
                                 4, R = CH_3

Complexes **3** and **4** react with maleic anhydride or fumaronitrile to give the stable anionic carbyne complexes $NEt_4[Cl_2(py)-(CO)(alkene)W\equiv CR]$, **5–8** (eq 2), which are isolated as non-

$$\left[\underset{Cl-\underset{\underset{O}{C}}{\overset{Cl}{\underset{\diagup}{W}}}\underset{\underset{O}{C}}{\equiv}CR}{\overset{py}{}}\right]^- \xrightarrow[CH_2Cl_2]{alkene,\ -CO} \left[\underset{Cl-\underset{\underset{O}{C}}{\overset{py}{\underset{\diagup}{W}}}\underset{}{\equiv}CR}{\overset{}{}}\right]^- \quad (2)$$

5, R = C_6H_5; alkene = maleic anhydride
6, R = CH_3; alkene = maleic anhydride
7, R = C_6H_5; alkene = fumaronitrile
8, R = CH_3; alkene = fumaronitrile

crystalline solids in 40–80% yield by extraction of the reaction residue with tetrahydrofuran (THF) and addition of ether to the reduced extracts.[10,11] Only the isomers containing the two chloride

(8) **3**: IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1965 (s), 1867 (s); ^{13}C NMR (ppm, $CDCl_3$) 267.2 (*C*Ph), 224.2 (CO), 221.8 (CO). **4**: IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1961 (s), 1857 (s); ^{13}C NMR (ppm, CD_2Cl_2) 277.6 (*C*CH$_3$), 222.8 (CO), 219.9 (CO).
(9) Labile anionic dihalotricarbonyltungsten carbyne complexes have previously been observed. Fischer, H.; Seitz, F. *J. Organomet. Chem.* **1984**, *268*, 247–258.
(10) **5**: IR (cm^{-1}, CH_2Cl_2) ν_{CO} 2041 (m), $\nu_{C=O}$ 1796 (m), 1728 (s); ^1H NMR (ppm, $CDCl_3$) 4.13 (d), 2.93 (d) (*J* = 5.0 Hz) (CH=CH); ^{13}C NMR (ppm, $CDCl_3$) 273.5 (*C*Ph), 206.8 (CO), 175.3, 174.6 (*C*=O), 51.5 (d, J_{CH} = 177 Hz), 50.2 (d, J_{CH} = 175 Hz) (*C*=C). **6**: IR (cm^{-1}, CH_2Cl_2) ν_{CO} 2037 (s), $\nu_{C=O}$ 1793 (s), 1727 (s); ^1H NMR (ppm, $CDCl_3$) 3.99 (d), 2.79 (d) (*J* = 4.9 Hz) (CH=CH); ^{13}C NMR (ppm, $CDCl_3$) 285.6 (*C*Me), 207.2 (CO), 175.2, 174.7 (*C*=O), 49.8 (d, J_{CH} = 177 Hz), 47.9 (d, J_{CH} = 176 Hz) (*C*=C). **7**: Two diastereomers; IR (cm^{-1}, CH_2Cl_2) ν_{CO} 2210 (m), ν_{CO} 2046 (s); ^1H NMR (ppm, $CDCl_3$) 3.07 (d), 3.00 (d) (*J* = 8.8 Hz), 3.06 (d), 2.08 (d) (*J* = 9.0 Hz) (CH=CH); ^{13}C NMR (ppm, $CDCl_3$) 271.6, 270.4 (*C*Ph), 208.8, 207.1 (CO), 30.9 (d, J_{CH} = 164 Hz), 30.6 (d, J_{CH} = 184 Hz), 28.8 (d, J_{CH} = 166 Hz), 27.9 (d, J_{CH} = 185 Hz). **8**: Two diastereomers; IR (cm^{-1}, CH_2Cl_2) ν_{CN} 2208 (m), ν_{CO} 2037 (s). ^1H NMR (ppm, $CDCl_3$) 2.92 (d), 2.82 (d) (*J* = 8.3 Hz), 2.80 (d), 1.97 (d) (*J* = 8.5 Hz) (CH=CH); ^{13}C NMR (ppm, $CDCl_3$) 285.1, 281.2 (*C*Me), 210.0, 207.7 (CO), 33.3, 29.9, 28.0, 26.6 (*C*=C).

ligands trans to the carbyne and the alkene, respectively, and the pyridine ligand trans to carbon monoxide are obtained.[12,13]

The neutral complex Cl(CO)$_2$(py)$_2$W≡CPh (1) reacts with maleic anhydride and fumaronitrile in THF to afford the neutral complexes Cl(py)$_2$(CO)(alkene)W≡CPh, 9 and 10 (9, alkene = maleic anhydride; 10, alkene = fumaronitrile), in 70–90% yield.[14] Complex 1 is significantly less reactive than its anionic counterpart 3. A large excess (10 equiv) of the alkenes and slightly elevated temperatures (40–50 °C) are required for this reaction to proceed at convenient rates.

The molecular structure of the maleic anhydride complex 9 is shown in Figure 1.[15] It is that expected[16] for a chloro tungsten carbyne complex containing two donor ligands (py) and two acceptor ligands (maleic anhydride and carbon monoxide) with the chloride trans to the carbyne and the pyridine ligands trans to maleic anhydride and CO. The alkene double bond is perpendicular relative to the tungsten–carbyne bond[17] thus maximizing π-bonding to the metal of both the alkene and the carbyne ligand. The anhydride group of maleic anhydride is oriented toward the carbyne ligand.

The most surprising feature in the reactions leading to the tungsten alkene carbyne complexes is the facile loss of carbon monoxide—normally, substitution of a carbonyl ligand in bissubstituted tungsten carbyne complexes X(CO)$_2$(L)$_2$W≡CR is difficult.[18] Therefore, we postulate an indirect mechanism for the substitution of carbon monoxide (eq 3). In the first step one
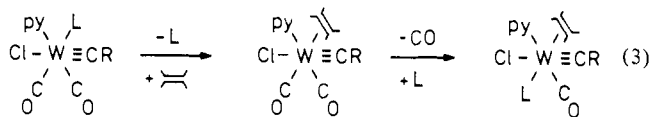
of the donor ligands (L = Cl⁻, py) is substituted by the alkene ligand affording a neutral intermediate with the alkene ligand trans to one of the two carbon monoxide ligands. Subsequently, the CO trans to the strongly π-bonding alkene is labilized and substituted by the ligand L (L = Cl⁻, py) giving rise to the observed products. Faster reaction of the anionic complexes 3 and 4 over the neutral complex 1 indicates that the first step is rate-determining. Lack of reaction of unactivated alkenes may be associated with the second step. Labilization of CO apparently is only achieved by electron-poor olefins such as maleic anhydride or fumaronitrile.

(11) Elemental analyses have been obtained for the new tungsten complexes 5–10.

(12) The cis arrangement of the alkene and pyridine ligands in 5–8 is confirmed by NOE difference spectroscopy. Irradiation of an NMR sample of 5 at the resonance frequency of the pyridine α-protons at 9.43 ppm leads to an increase in intensity of the alkene proton signal at 2.93 ppm.

(13) The fumaronitrile complexes 7 and 8 as well as 10 are obtained as mixtures of diastereomers (approximately 1:1) due to coordination of the enantiotopic faces of fumaronitrile to the asymmetric complex fragments Cl(CO)(py)(L)W≡CR in 7 and 8 (L = Cl⁻) as well as 10 (L = py).

(14) 9: IR (cm⁻¹, CH$_2$Cl$_2$) ν_{CO} 2044 (s), $\nu_{C=O}$ 1806 (s), 1738 (s); ¹H NMR (ppm, CDCl$_3$) 4.42 (d), 3.19 (d) (J = 5.3 Hz) (CH=CH); ¹³C NMR (ppm, CDCl$_3$) 268.0 (CPh), 207.1 (CO), 175.3, 173.4 (C=O), 55.4 (d, J_{CH} = 180 Hz), 51.8 (d, J_{CH} = 177 Hz) (C=C). 10: Two diastereomers; IR (cm⁻¹, CH$_2$Cl$_2$) ν_{CN} 2218 (m), ν_{CO} 2049 (s); ¹H NMR (ppm, CDCl$_3$) 3.41 (d), 3.32 (d) (J = 9.2 Hz), 3.36 (d), 2.39 (J = 9.2 Hz) (CH=CH); ¹³C NMR (ppm, CDCl$_3$) 264.7, 264.3 (CPh), 208.2, 206.7 (CO), 35.4, 33.7, 32.6, 30.0 (C=C).

(15) Cl(CO)(maleic anhydride)(py)$_2$W≡CPh (9, monoclinic, P2$_1$/n, a = 11.522 Å (2) b = 16.026 (3) Å, c = 11.680 (2) Å, β = 102.97 (1)°, V = 2101.7 (6) Å³, Z = 4, μ(Mo Kα) = 59.8 cm⁻¹, ρ(calcd) = 1.87 g cm⁻³, T = 23 °C. Of 4045 absorption corrected reflections collected, 4° ≥ 2θ ≥ 50°, 3698 were unique and 3218 with F_o ≥ 3σ(F_o) were used in the solution (heavy atom) and refinement (blocked cascade) of the structure. All non-hydrogen atoms anisotropic, hydrogen atoms idealized. R_F = 3.28%; R_{wF} = 3.56%; GOF = 1.51; highest peak, final difference map, 0.98 e Å⁻³ (1.01 Å from W).

(16) Huttner, G.; Frank, A.; Fischer, E. O. Isr. J. Chem. 1976/1977, 15, 133–142.

(17) Orthogonal bonding arrangement of an alkene and a metal–carbon triple bond was also observed in W(CAl$_2$Me$_4$Cl)(PMe$_3$)$_2$(CH$_3$)(C$_2$H$_4$). Churchill, M. R.; Wasserman, H. J. Inorg. Chem. 1981, 20, 4119–4123.

(18) Unpublished observations.

Efficient Asymmetric Synthesis of (+)-Mesembrine and Related Chiral 4,4-Disubstituted Cyclohexanones

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Received July 11, 1985

In spite of the numerous racemic total syntheses[1] of the *Sceletium* alkaloid mesembrine 1, there is yet to be described in the literature a true asymmetric approach to this substance. In 1973 Yamada and Otani[2] reported a synthesis enriched in the (+) enantiomer of 1 in 25–30% ee via an optically active proline derivative and more recently Takano[3] reported an enantioselective synthesis of naturally occurring (–)-mesembrine. However, the latter work, originating from D-mannitol, was of an indirect nature wherein none of the stereocenters of mannitol were carried through to the final product. Instead a chiral intermediate was prepared, which was brought forward to the target via well-known procedures. Our recent interest[4,5] in asymmetric synthesis of compounds containing quaternary carbon centers with specific stereochemistry has led us to consider mesembrine as a viable target via 4,4-disubstituted cyclohexanones 2, which could be derived from the

(+)-1   2, Ar = 3,4-(MeO)$_2$Ph   3
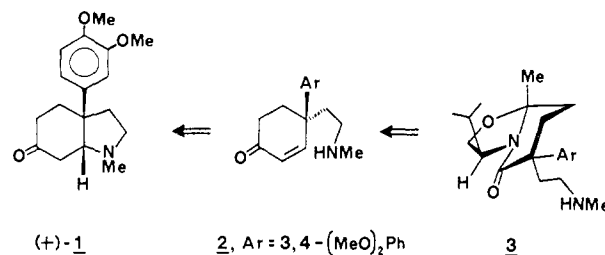
chiral, nonracemic, bicyclic lactam 3. Previously we described the synthetic value of the [3.3.0]-bicyclic lactams 4 and 5 as precursors to 2,2-disubstituted keto acids 7[4] and 4,4-disubstituted cyclopentenones 8[5] by sequential alkylation to the bicyclic lactams 6 in very high enantiomeric purity (Scheme I).

We now report that it is feasible to prepare [4.3.0]-bicyclic lactams and sequentially alkylate them to the key intermediate 3 which led to an efficient synthesis of (+)-mesembrine in 23% overall yield and in >98% enantiomeric excess.

The requisite keto acid (±)-9 was prepared from the dilithio salt of (3,4-dimethoxyphenyl)acetic acid and 2-methyl-2-(2-iodoethyl)-1,3-dioxolane[6] (2 equiv of BuLi, 0–30 °C, THF) and acidified (EtOH, pyridinium–TsOH, 60 °C) to cleave the ketal furnishing 9 in 85% yield (mp 72–74 °C). Treatment of (±)-9

(1) The synthesis of (±)-mesembrine has been described by a number of laboratories: Kochhar, K. S.; Pinnick, H. W. Tetrahedron Lett. 1983, 24, 4785. A complete bibliography for previous syntheses is given therein.

(2) Otani, G.; Yamada, S.-I. Chem. Pharm. Bull. 1973, 21, 2130.

(3) Takano, S.; Imamura, Y.; Ogasawara, K. Tetrahedron Lett. 1981, 22, 4479.

(4) Meyers, A. I.; Harre, M.; Garland, R. J. Am. Chem. Soc. 1984, 106, 1146.

(5) Meyers, A. I.; Wanner, K. T. Tetrahedron Lett. 1985, 26, 2047.

(6) Stowell, J. C.; King, B. T.; Hauck, H. F., Jr. J. Org. Chem. 1983, 48, 5381.