ficiency exceeded 50% in most systems except the cases of aniline and isopropylamine.[26] The highest efficiency of 87.3% was obtained in the initial stage (5 h) of N-ethylation of benzylamine; prolonged irradiation (10 h) to yield *N*,*N*-diethylbenzylamine in this system decreased the efficiency to some extent (62.2%). Thus, only small amount of the byproducts, H_2 and carbonyl derivatives, remained because of the incorporation to the N-alkylated products.

Similar to platinized anatase TiO_2, CdS, and rutile TiO_2 (prepared by hydrolysis of titanium(IV) tetra-2-propoxide followed by calcination at 1000 °C in air) with 5 wt % of platinum black also exhibited the photocatalytic activity for the N-alkylation of amines (Table I); benzylamine was converted into *N*-ethylbenzylamine in ethanol solution. Consistent with the proposed reaction scheme the photocatalytic activity of several semiconductor powders was parallel to that for the dehydrogenation of alcohols. On the basis of this relationship, semiconductor materials with higher activities are now being explored.

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(26) The lower efficiency of N-alkylation of aniline may be attributed to the fact that *N*-ethylideneaniline in ethanol solution was little reduced in the dark under H_2 at room temperature even in the presence of Pt.

Reactions of Substituted Carbonyltungsten Carbyne Complexes with Dithiocarbamate Salts. Carbonyl Carbyne Coupling and Formation of Coordinated Thioaldehydes

Andreas Mayr,* Gregory A. McDermott, Alison M. Dorries, and Ann K. Holder

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

William C. Fultz and Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received June 11, 1985

Group 6[19] transition-metal carbyne complexes stabilized by nitrogen donor ligands, $X(CO)_2(L)_2M{\equiv}CR^1$ (X = halide; L = nitrogeneous ligand; M = Cr, Mo, W), combine thermal stability, coordinative lability, and high reactivity of the carbyne ligand. We have recently developed efficient and simple methods for their preparation[2] and have begun to investigate their chemistry. We made use of the coordinative lability of $Cl(CO)_2(py)_2W{\equiv}CR$ (**1**) (py = pyridine; **1a**, R = C_6H_5; **1b**, R = CH_3) in the synthesis of stable (alkene)tungsten carbyne complexes.[3] Here we wish to report about reactions of **1** with diethyldithiocarbamate salts, $Kat^+Et_2NCS_2^-$ (Kat = Na, H_2NEt_2). These reactions involve not only facile ligand substitution reactions but also transformations of the carbyne ligands which depend strongly on the nature of the counterion.

Reaction of $Cl(CO)_2(py)_2W{\equiv}CPh$ (**1a**) with 2 equiv of sodium diethyldithiocarbamate, NaS_2CNEt_2, in THF results in the formation of a green anionic product which was isolated as its tetraethylammonium salt **2** (eq 1).[4] Complex **2** contains two dithiocarbamate ligands, a carbonyl ligand, and a phenylketenyl ligand.[4] The compound evidently was formed by substitution of the two pyridine ligands and the chloro ligand in **1a** by two dithiocarbamate ligands and a coupling step between one carbonyl and the carbyne ligand.[5] The immediate precursor of **2** is presumably an anionic intermediate **3** containing one chelating and one monodentate dithiocarbamate ligand. Coupling is then induced by chelation of the second dithiocarbamate ligand.[6]

$$\underset{\mathbf{1a}}{\mathrm{Cl(CO)_2(py)_2W{\equiv}CPh}} \xrightarrow[\text{2. NEt}_4\text{Cl, CH}_2\text{Cl}_2]{\text{1. 2NaS}_2\text{CNet}_2\text{, THF}} \underset{\mathbf{2},\ 96\%}{\mathrm{NEt_4[(Et_2NCS_2)_2(CO)W(PhCCO)]}} \quad (1)$$

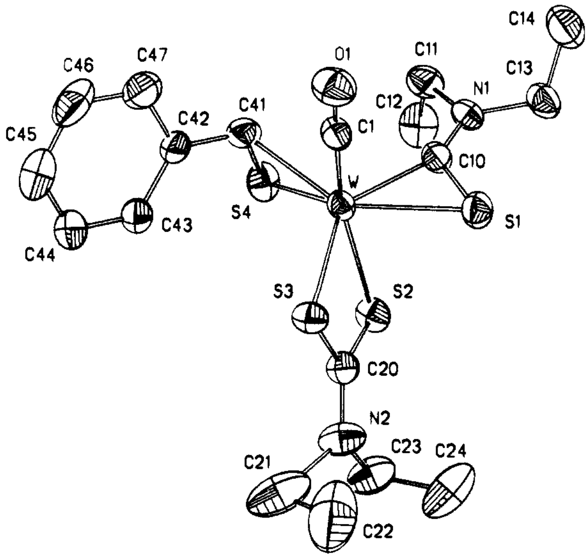
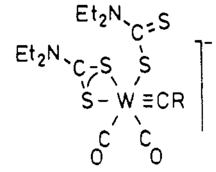


Figure 1. Molecular structure and labeling diagram for **4a**. W–C(1), 1.958 (6); W–C(10), 2.040 (6); W–C(41), 2.251 (6); W–S(1), 2.542 (2); W–S(2), 2.547 (2); W–S(3), 2.417 (2); W–S(4), 2.296 (2) Å. S(1)–W–C(10), 41.9 (2)°; C(1)–W–C(10), 87.0 (3)°; C(1)–W–S(1), 81.0 (2)°; S(2)–W–S(3), 70.6 (1)°; C(1)–W–S(2), 159.3 (2)°; C(1)–W–S(3), 95.7 (2)°; S(1)–W–S(3), 91.8 (1)°; C(1)–W–S(4), 113.5 (2)°; C(1)–W–C(41), 69.5 (2)°; S(1)–W–S(4), 148.0 (1)°; S(3)–W–S(4), 113.7 (1)°; W–S(4)–C(41), 66.1 (2)°.



3

In case the diethylammonium salt of the dithiocarbamate ligand is used in the reaction with **1**, the products formed are very different (eq 2). Again, 2 equiv of the ligand react with the metal complex, but the deep green products[7] **4** are neutral compounds

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(1) Fischer, E. O.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 805–815.

(2) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 609–610.

(3) Mayr, A.; Dorries, A. M.; McDermott, G. A.; Geibe, S. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 7775–7776.

(4) **2**: mp 84 °C dec. Anal. Calcd for $C_{27}H_{45}N_3O_2S_4W$: C, 42.91; H, 6.00; N, 5.56. Found: C, 42.34; H, 6.07; N, 5.95. IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1833 (vs), ν_{CCO} 1673 (m); ^{13}C NMR (ppm, $CDCl_3$) 234.9 (CO), 212.1, 210.3 ($Et_2N\mathit{C}S_2$), 201.7 (PhC*C*O), 187.9 (Ph*C*CO).

(5) Carbonyl–carbyne coupling reactions have been observed previously, for example: (a) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* **1976**, *88*, 649–650; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632–633. (b) Kreissl, F. R.; Sieber, W. J.; Alt, H. G. *Chem. Ber.* **1984**, *117*, 2527–2530. (c) Fischer, E. O.; Filippou, A. C.; Alt, H. G. *J. Organomet. Chem.* **1984**, *276*, 377–385. (d) Churchill, M. R.; Wassermann, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768. (e) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483. (f) Reference 15d.

(6) Dithiocarbamate-induced carbonyl–carbyne coupling has been observed in $Et_2NCS_2(CO)_2(Ph_2PCH_2CH_2PPh_2)WCCH_2Ph$.[5e]

(7) **4a**: mp 138–144 °C dec. Anal. Calcd for $C_{18}H_{26}N_2OS_4W$: C, 36.12; H, 4.38; N, 4.68; S, 21.43. Found: C, 36.05; H, 4.48; N, 4.99; S, 20.73. IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1925 (s), ν_{Et_2NCS} 1526 (s), $\nu_{Et_2NCS_2}$ 1509 (s); ^1H NMR (ppm, $CDCl_3$) 5.42 (*H*CSPh); ^{13}C NMR (ppm, $CDCl_3$) 256.9 (J_{CW} = 111 Hz, $Et_2N\mathit{C}S$), 217.5 (J_{CW} = 151 Hz, CO), 214.6 ($Et_2N\mathit{C}S_2$), 57.0 (J_{CH} = 173 Hz, H*C*SPh). **4b**: mp 82–86 °C. Anal. Calcd for $C_{13}H_{24}N_2OS_4W$: C, 29.11; H, 4.48; N, 5.23; Found: C, 29.88; H, 4.83; N, 4.98. IR (cm^{-1} CH_2Cl_2); ν_{CO} 1913 (s), ν_{Et_2NCS} 1525 (s), $\nu_{Et_2NCS_2}$ 1509 (s); ^1H NMR (ppm, $CDCl_3$) 4.58 (9, *H*CSMe), 2.16 (d, J_{HH} = 5.76 Hz, $HCSC\mathit{H}_3$); ^{13}C NMR (ppm, $CDCl_3$) 256.6 (J_{CW} = 108 Hz, $Et_2N\mathit{C}S$), 217.9 (J_{CW} = 147 Hz, CO), 54.8 (d, J_{CH} = 175 Hz, H*C*SMe), 30.6 (q, J_{CH} = 128 Hz, $HCS\mathit{C}H_3$).

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due to the uptake of a proton. This proton is bonded to the former carbyne carbon as part of a thioaldehyde ligand. Evidently, the proton originates from the diethylammonium counterion and the sulfur atom of the thioaldehyde ligand is generated by cleavage of a diethyldithiocarbamate ligand into diethylthiocarboxamide and sulfide.

$$1 \xrightarrow[\text{THF}]{2[H_2NEt_2][S_2CNEt_2]} (Et_2NCS_2)(Et_2NCS)W(CO)(RCHS) \quad (2)$$

4a R = C_6H_5; 96%

4b, R = CH_3; 62%

The molecular structure of **4a** is shown in Figure 1.[8] The coordination geometry of the tungsten atom can be described as a trigonal bipyramid with the carbonyl ligand and one dithiocarbamate sulfur atom (S2) as the axial ligands. The equatorial positions are occupied by thiobenzaldehyde, diethyl thiocarboxamide,[9] and the second sulfur atom (S3) of dithiocarbamate.[10,11]

The mechanism of formation of the novel complexes **4** is unknown at this point. However, we assume that, as in reaction 1, initially anionic intermediates with two dithiocarbamate ligands, **3**, form. In these intermediates the carbyne carbon may be sufficiently basic to accept a proton[15] from the diethylammonium counterion, $H_2NEt_2^+$, with concomitant addition of the noncoordinated sulfur atom to the metal center affording bis(dithiocarbamate)tungsten dicarbonyl alkylidene complexes, $(Et_2NCS_2)_2(CO)_2W{=}CHR$. Loss of carbon monoxide followed by cleavage of one dithiocarbamate ligand and transfer of a sulfur atom to the alkylidene ligand would result in formation of the thioaldehyde ligands. This is the first reported reaction to provide access to aromatic as well as aliphatic thioaldehyde ligands.[16-18]

Acknowledgment. This work was supported by an Atlantic Richfield Foundation Grant of Research Corporation and by the National Science Foundation (CHE-8411023). We thank Professor J. L. Templeton for making a manuscript of his work available to us prior to publication.[5e]

Supplementary Material Available: Crystallographic data for **4a**: atomic coordinates (Table 1S), bond distances (Table 2S), bond angles (Table 3S), anisotropic temperature factors (Table 4S), hydrogen atom coordinates (Table 5S), and observed vs. calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(8) $C_{19}H_{26}N_2O_2S_4W$ (**4a**): monoclinic, $P2_1/n$, $a = 11.224$ (1) Å, $b = 17.078$ (2) Å, $c = 12.221$ (1) Å, $\beta = 99.21$ (1)°, $Z = 4$, $V = 2312.1$ (4) Å^3, D(calcd) = 1.80 g cm^{-3}, μ(Mo K$_\alpha$) = 56.4 cm^{-1}. Collected 4528 reflections ($4° \leqslant 2\theta \leqslant 50°$); 4070 reflections unique and 3636 absorption corrected reflections considered observed ($F_o \geqslant 2.5\sigma(F_o)$) were used in the solution (direct) and refinement (blocked cascade) using anisotropic thermal parameters for all non-hydrogen atoms (hydrogen atoms idealized). $R_F = 3.78\%$, $R_{wF} = 4.45\%$, GOF = 1.34.

(9) For other structurally characterized examples of thiocarboxamido ligands arising from cleavage of dithiocarbamate ligands, see: (a) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182–2186. (b) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599–2605.

(10) A related sulfido(thiocarboxamido) complex W(S)-$(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$ was spectroscopically characterized. Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745–750.

(11) The arrangement of the ligands can be rationalized in terms of maximal π-bonding. In trigonal-bipyramidal geometry four d-orbitals are available for π-bonding, xz, yz, "xy", and "$x^2 - y^2$".[12,13] The diethylthiocarboxamido ligand interacts with the "xy" orbital and, less strongly, with yz. The thioaldehyde ligand bonds to the xz orbital and carbon monoxide interacts with xz and yz. The "$x^2 - y^2$" orbital, being empty, can accept electrons from the filled p-orbital of the equatorial sulfur atom. This sulfur to metal π-donation is reflected in the short W–S3 distance.[14]

(12) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365–374.

(13) In the (idealized) trigonal bipyramid the z axis is chosen to coincide with the trigonal axis (axial ligands) and the y axis to coincide with one of the 2-fold axes (one equatorial ligand).

(14) π-Donation by dithiocarbamate ligands in electron-deficient complexes has been discussed by Templeton. Templeton, J. L.; Winston, P. B.; Ward, C. B. *J. Am. Chem. Soc.* **1981**, *103*, 7713–7721.

(15) For protonation reactions of carbyne ligands, see: (a) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570–6571. (b) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322–6329. (c) Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493–495. (d) Howard, J. A. K.; Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A.; Stringer, A. *Inorg. Chim. Acta* **1985**, *100*, 23–32. (e) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem.* **1984**, *96*, 618–619; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640. (f) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. *J. Organomet. Chem.* **1984**, *270*, C45–C47. (g) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124–1126.

(16) Transformation of benzylidene ligands into thiobenzaldehyde ligands occurs in the reaction of $(CO)_5W{=}CHAr$ with SCN$^-$ or elemental sulfur, S_8. Fischer, H.; Zeuner, S. *Z. Naturforsch., B* **1985**, *40B*, 954–960.

(17) Thioaldehyde ligands have previously been prepared by reaction of $(CO)_5WSH^-$ with benzaldehydes or corresponding Schiff bases. Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604–5608.

(18) For the synthesis of a thioformaldehyde ligand by sulfur addition to a terminal methylene ligand, see: Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939–5940.

(19) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Reductive Coupling of Two Carbon Monoxide Ligands To Form a Coordinated Alkyne

Patricia A. Bianconi, Ian D. Williams, Mary P. Engeler, and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received September 10, 1985

An important goal in C_1 chemistry has been to promote C–C bond formation using carbon monoxide as substrate. Reductive coupling of CO to give carbon–carbon multiply bonded fragments has been previously reported, in which oxygen is ultimately attached to a transition, lanthanide, or actinide metal.[1] Reduction of CO by alkali metals to produce $(M^+)(^-OC{\equiv}CO^-)(M^+)$ and its oligomers[2] and reduction of iron pentacarbonyl to form a coordinated butadiene[3] have also been described. Previously we achieved reductive coupling of alkyl isocyanides to give coordinated bis(alkylamino)acetylenes and removal of the ligand as RNHC(O)C(O)NHR, with the newly formed carbon–carbon bond intact.[4] Study of this reaction led to the identification of four factors that promote reductive coupling: (i) high coordination number with use of linear or chelating ligands;[4] (ii) molecular geometry in which the orbitals involved in the coupling reaction are properly aligned;[5] (iii) an electron-rich metal center;[6] (iv) Lewis acid coordination of the heteroatoms of the ligands to be coupled.[4,7] Here

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(1) (a) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (c) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712. (d) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959. (e) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. (f) Gambarota, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (g) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706. (h) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (i) Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774.

(2) (a) Weiss, E.; Buechner, W. *Helv. Chim. Acta* **1963**, *46*, 1121; **1964**, *47*, 1415. (b) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

(3) (a) Nasta, M. A.; MacDiarmid, A. G.; Saalfeld, F. E. *J. Am. Chem. Soc.* **1972**, *94*, 2449. (b) Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1684.

(4) (a) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617. (b) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263. (c) Warner, S.; Lippard, S. J., unpublished results.

(5) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.

(6) Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860.