

atom, the usual coordination for thiourea, and through a carbon atom of one of the methyl groups. Formation of the two metal-carbon bonds appears to be accompanied by loss of molecular hydrogen.

The X-ray structure revealed a nearly perfect octahedron, all of the angles around the platinum being close to 90°. However, some peculiarities are worth noting: the PtS(1)C(1) and PtS(2)C(2) angles (98°40 and 98°92) are equivalent to one another but clearly different from M-S-C bond angles observed in other tetramethylthiourea metallic complexes, e.g., 109°2 for a copper complex (3) and 105°8 for a cobalt complex.⁹ This decreased angle is accounted for by the steric constraints imposed on the ligand by the formation of the metal-carbon bond.

Moreover some important nonequivalences appear in the bond lengths and angles of the two tmtu groups. The C(13) atom is 0.24 Å out of the PtS(1)C(1)N(3)N(1) plane while Pt, S(2), C(2), and C(14) are coplanar and in this ring the N(4) atom is 0.11 Å out of plane. This different nonplanarity induces important inequivalences in bond lengths; the N(3)C(13) bond (1.367 Å) is significantly shorter than the N(4)C(14) (1.475 Å) while C(1)N(3) (1.385 Å) is significantly longer than C(2)N(4) (1.334 Å). Finally the Pt-S bonds had a mean length of 2.31 Å, which agrees well with those found in Pt(II) thiourea complexes;¹⁰ apparently the Pt-S bond is not greatly perturbed by the higher oxidation state of platinum.

The ¹³C=S and ¹⁵N chemical shifts of tetramethylthiourea are quite different from those of other thioureas in which the nitrogen lone pair electrons may be delocalized through thiol-thione tautomerization.¹¹ The relative localization of electrons on the thione and the amine of tmtu may provide flexibility around the C-N bond which facilitates the nonplanarity observed for the ligands in the X-ray structure.

Internal cyclometalation of nitrogen or phosphorous donor ligands by transition metals has been quite extensively investigated. Many of the complexes involve metalation of a phenyl ring,¹²⁻¹⁵ a significant number involve metalation of an alkyl group,¹⁶ and activation of an aldehyde carbon-hydrogen bond has been reported.¹⁷ A few examples exist involving a sulfur donor ligand,^{18,19} but to our knowledge the present report is the first cyclometalation of a thiourea ligand. In most cases cyclometalation involves the formation of a five-membered ring as in the present molecule.

An important difference between these reactions and the one that we have observed must be emphasized. In previous cases, the reaction occurs by electrophilic substitution followed by elimination of, for example, HX where X = Cl or Br. In our case, the halide is not eliminated; rather, the metal is oxidized and molecular hydrogen is the leaving group. The loss of molecular hydrogen has been observed for cyclometalation of a ruthenium hydride complex containing a phosphorous ligand in which oxidative addition of a hydrogen atom on the metal is followed by a reductive elimination.²⁰ This type of hydride intermediate seems unlikely in our case since the simultaneous addition of two tmtu hydrogen atoms to the platinum would require a metal with an oxidation number of VI surrounded by 20 electrons.

In conclusion, we report a cyclometalation reaction that leads to a change in the coordination number and oxidation state of the metal and therefore can be considered as an oxidative addition. Further work is in progress to investigate the full scope of this reaction and its application to other systems.

Registry No. tmtu, 2782-91-4; [Pt(tmtu)Br₂]₂, 97487-67-7; Pt(tmtu)₂Br₂, 97521-29-4; K₂PtBr₂, 13826-94-3.

Supplementary Material Available: Listings of angles (Table S₁), bond distances (Table S₂), positional parameters, and their estimated standard deviations (Table S₃) for Pt(tmtu)₂Br₂ (4 pages). Ordering information is given on any current masthead page.

One- and Two-Electron Reduction of a Chromium(0) Alkyne Complex and Isolation of the Chromium(1-) Product

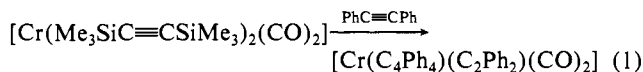
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We have recently provided evidence¹ that alkynes, like alkenes,² are sufficiently good π-acceptor ligands to form transition-metal complexes, analogous to carbonylmetalates, in which the metal has a negative oxidation state. It is also well established that the presence of two π-bonds between the carbon atoms allows alkynes to act as electronically flexible ligands, donating between two and four electrons to transition-metal centers.^{3,4} We now wish to report an example of a Cr(0) alkyne complex in which these characteristics allow two successive reversible one-electron reductions to a Cr(2-) complex without loss of a coordinated ligand and permit the isolation and characterization of the remarkably stable Cr(1-) intermediate.

The substrate for reduction was prepared by reacting [Cr(Me₃SiC≡CSiMe₃)₂(CO)₂]⁵ with diphenylacetylene in pentane (eq 1). The precipitated product was obtained as a green mi-



crocrystalline powder by recrystallization from toluene/pentane and formulated as [Cr(C₄Ph₄)(C₂Ph₂)(CO)₂] (1) primarily on the basis of ¹³C NMR and infrared spectroscopy.⁶ The chemical

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shift of the singlet at δ 199.1 assigned to the acetylenic carbons indicated the presence of a diphenylacetylene ligand acting as a four-electron ligand,⁴ while coupling of two diphenylacetylene ligands to form a cyclobutadiene ligand was indicated by the presence of an absorption at δ 94.7 which lacked ¹H coupling and had the appropriate integrated intensity in uncoupled spectra.⁷

Reduction of **1** was explored electrochemically through cyclic voltammetry of a 10^{-3} M solution in tetrahydrofuran (THF) with 0.5 M $[\text{NBu}_4][\text{ClO}_4]$ as supporting electrolyte. The complex underwent chemically reversible reductions at -1.09 and -1.88 V (vs. SCE) for which the ΔE_p (65 and 66 mV) approached those expected for reversible one-electron couples,⁸ suggesting that the species present were $\mathbf{1}^-$ and $\mathbf{1}^{2-}$ and that neither reduction resulted in ligand dissociation.

The two successive one-electron reductions can be carried out chemically by alkali naphthalenide reduction in THF. For example, addition of 1.6 mL of a ca. 0.044 M solution of potassium naphthalenide to a solution of 0.045 g (0.07 mmol) of **1** in 3 mL of THF gives, in the presence of excess dibenzo-18-crown-6 (DBC), a solution with IR absorptions at 1907 and 1840 cm^{-1} assigned to the $\text{C}=\text{O}$ stretches of $\mathbf{1}^-$. The concomitant color change from green-brown to dark khaki was followed by further darkening to an intense red-brown as a second equivalent of reductant was added to form $\mathbf{1}^{2-}$. The spectrum of the final solution contained two strong carbonyl absorptions at 1791 and 1669 cm^{-1} and a band at 1735 cm^{-1} assigned to the $\text{C}\equiv\text{C}$ stretching absorption.⁹ The identity of $\mathbf{1}^{2-}$ was confirmed by its ¹³C NMR spectrum, which established that the complex retained the tetraphenylcyclobutadiene and diphenylacetylene ligands.¹¹

The radical anion $\mathbf{1}^-$ is remarkably stable. Reduction of 18-electron complexes with carbonyls and other π -acceptor ligands sometimes proceeds in one-electron steps,¹² but the radical intermediates are typically highly reactive. We have, however, been able to isolate thermally stable crystalline salts of $\mathbf{1}^-$ from solutions prepared by reduction of ca. 0.02 M **1** in THF with 0.08–0.15 M potassium naphthalenide in the presence of an equivalent of DBC. The solvent is removed and the product first extracted into toluene and then crystallized at -60 °C. Recrystallization from a concentrated THF solution at room temperature by stepwise addition of diethyl ether (4-fold excess) typically gives black needles of $[\text{K}(\text{DBC})]\cdot 2\text{THF}$ in 30% yield;¹³ on one occasion, however, we also observed the formation of small black prisms more suitable for X-ray diffraction studies which were shown to be a monosolvate of $\mathbf{1}^-$ with a DBC complexed K^+ counterion.^{14,15}

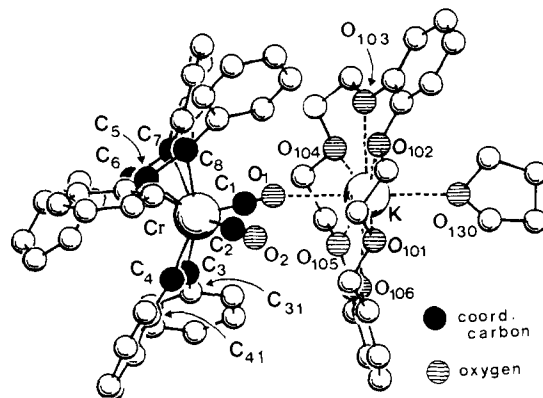


Figure 1. SNOOPI drawing of $[\text{K}(\text{DBC})]\cdot\text{THF}$.¹⁵ All atoms are drawn at 50% of their covalent radii. Hydrogen atoms and the minor orientation of the THF omitted for clarity. Selected bond distances (Å) and angles(deg): Cr–C(1) 1.850 (7); Cr–C(2) 1.848 (8); C(1)–O(1) 1.159 (7); C(2)–O(2) 1.164 (8); Cr–C(3) 2.072 (7); Cr–C(4) 2.016 (7); Cr–C(cbd) (av) 2.16; C(3)–C(4) 1.29 (1); C(5)–C(6) 1.46 (1); C(6)–C(7) 1.46 (1); C(7)–C(8) 1.46 (1); C(8)–C(5) 1.47 (1); K–O(1) 2.764 (5); K–O(DBC) (av) 2.75; C(1)–Cr–C(2) 97.4 (3); Cr–C(1)–O(1) 178.2 (6); Cr–C(2)–O(2) 179.6 (6); C(1)–O(1)–K 146.4 (5); C(3)–C(4)–C(41) 140.0 (7); C(4)–C(3)–C(31) 143.6 (7). The ipso carbons are bent back from the carbons of the cbd plane as follows (deg): C(5) 10.6 (5); C(6) 0.4 (5); C(7) 13.2 (5); C(8) 13.4 (5).

The principal features of the structure of $\mathbf{1}^-$ and of the interaction of $\mathbf{1}^-$ with the counterion in the monosolvate are illustrated in Figure 1. The oxygen atom of one of the carbonyl ligands of $\mathbf{1}^-$ occupies a K^+ coordination site, but this isocarbonyl interaction¹⁷ is apparently weak and does not result in any observable differences between the geometries of the two carbonyl ligands.^{18,19} The plane bisecting the C_1CrC_2 angle bisects the alkyne ligand, which is almost perpendicular to this plane (actual angle 77°).

One reasonable explanation of why **1** can be reduced to $\mathbf{1}^-$ and then to $\mathbf{1}^{2-}$ without ligand loss is that the added electrons are placed in a metal orbital that is antibonding with respect to one of the pairs of alkyne π -electrons, i.e., that the alkyne in $\mathbf{1}^{2-}$ effectively acts as a two-electron ligand rather than as a four-electron ligand as in **1**. Comparison of the ¹³C NMR spectra of the two molecules^{6,11} shows that this is indeed the case: in $\mathbf{1}^{2-}$ the absorption of the acetylenic carbons in $\mathbf{1}^{2-}$ is a full 60 ppm upfield of the corresponding resonance of **1** and has shifted from the region characteristic of four-electron alkynes into that characteristic of

(6) Selected IR (THF) 2000 s, 1950 s cm^{-1} ; ¹³C[¹H] NMR (75.5 MHz, C_6D_6) δ 241.8 (CO), 199.1 (C_2Ph_2), 94.7 (C_4Ph_4); the phenyl resonances were observed in the range δ 140–120. Anal. Calcd for $\text{C}_{44}\text{H}_{30}\text{CrO}_2$: C, 82.20; H, 4.70. Found: C, 82.66, H, 4.69.

(7) For ¹³C NMR spectra of other phenyl-substituted cyclobutadiene complexes, see: (a) Hoberg, H.; Fröhlich, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 145. (b) Seyferth, D.; Merola, J. S.; *J. Organomet. Chem.* **1978**, *160*, 275. (c) Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* **1982**, *1*, 812. (d) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, G. E. *J. Chem. Soc., Dalton Trans.* **1984**, 1141. (e) Hughes, R. P.; Reish, J. W.; Rheingold, A. L. *Organometallics* **1984**, *3*, 1761.

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(9) IR spectra of $\mathbf{1}^-$ and $\mathbf{1}^{2-}$ in solutions containing Kryptofix-222,¹⁰ which should minimize the effects of interactions with the counterion on the stretching absorptions of the carbonyl ligands, are similar to spectra in solutions containing DBC: $\mathbf{1}^-$, 1905 s, 1840 s, 1740 w, 1715 w cm^{-1} ; $\mathbf{1}^{2-}$, 1800 ms, 1740 ms, 1700 ms cm^{-1} .

(10) Kryptofix-222 is a proprietary name for the cryptand 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane as sold by E M Science.

(11) ¹³C NMR (75.5 MHz, THF) δ 270.5 (CO), 138.6 (C_2Ph_2), 81.3 (C_4Ph_4); crown ether, naphthalene, and phenyl resonances were also observed. No ¹³C NMR spectrum could be observed without a slight excess of naphthalenide, which probably suppressed self-exchange reactions.

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(13) Anal. Calcd For $\text{C}_{72}\text{H}_{70}\text{CrKO}_{10}$: C, 72.88; H, 5.61. Found (Galbraith): C, 72.62; H, 5.84. IR (Nujol mull, selected bands) 1897 s, 1830 s, 1750 w, 1735 vw cm^{-1} .

(14) Although the bisolvate needles are less suitable for diffraction studies than the monosolvate prisms, we have confirmed the identity of the bisolvate by an independent diffraction study which establishes that the structures of the anions and their interactions with the $[\text{K}(\text{DBC})]^+$ counterion are indistinguishable in the two solvates. The second THF molecule has no bonding interactions with either the cation or the anion. Wink, D. J.; Cooper, N. J., unpublished results.

(15) Monoclinic space group $P2_1/n$, $Z = 4$, $a = 14.711$ (4) Å, $b = 26.357$ (6) Å, $c = 15.417$ (3) Å, $\beta = 96.96$ (2)°, $V = 5964$ (6) Å³, $d_c = 1.24$ g cm^{-3} , $d_0 = 1.25$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ Å. Of 15643 reflections measured (some as ω and 2θ scans) in the range $3.5^\circ < 2\theta < 50^\circ$, 4305 unique data had $I > 3.0\sigma(I)$ and were used in structure solution (by direct methods using SHELXTL^{16a}) and refinement (using the Oxford CRYSTALS program^{16b}). Refined batchscales of 1.18 and 0.82 were applied to the 2θ and ω scans. Least-squares refinement with a block-diagonalized matrix converged to a final $R = 6.66\%$ and $R_w = 6.30\%$. Disorder of the THF was modeled with two orientations having refined occupancies of 0.683 and 0.317.

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(19) The Nujol mull IR spectrum of $[\text{K}(\text{DBC})]\cdot 2\text{THF}$ ¹⁴ established that the isocarbonyl interaction is too weak to produce a significant perturbation of the carbonyl stretching absorptions at 1897 and 1830 cm^{-1} (cf. ref 9). The solid-state IR spectrum of $[\text{K}(\text{DBC})]\cdot\text{THF}$ was not obtained because of the limited availability of the material.

