

necessarily preferred. Since Br (and CH₃) have larger packing radii, structure determinations on [Os₂Br₈]²⁻ (and [Os₂(CH₃)₈]²⁻ if it can be prepared) would be of special interest. Efforts are currently under way to do this and, at the same time, determine the structures of other salts of [Os₂Cl₈]²⁻ in order to establish the influence of crystal packing on the rotational geometry found in the solid state.

Studies on the reaction chemistry of (PPN)₂Os₂Cl₈ have been carried out. Its reaction with refluxing 10:1 acetic acid/acetic anhydride mixtures for 12 h regenerates Os₂(O₂CCH₃)₄Cl₂ in 71% yield. Monodentate phosphines react almost instantaneously with (PPN)₂Os₂Cl₈ in ethanol at room temperature to produce the mononuclear *trans*-[OsCl₄(PR₃)₂]⁻ anions in essentially quantitative yield (PR₃ = PMe₃, PEt₃, P-*n*-Pr₃, P-*n*-Bu₃, PMePh₂, PMe₂Ph, and PPh₃). These anions react further with excess phosphine in refluxing ethanol (4-6 h) to produce the yellow osmium(II) complexes OsCl₂(PR₃)₄ (PR₃ = PMe₃ or PMe₂Ph) or [Os₂(μ-Cl)₃(PR₃)₆]⁺ (PR₃ = PEt₃, P-*n*-Pr₃, P-*n*-Bu₃, or PMePh₂; isolated as their PF₆⁻ salts)²⁴ in yields up to 80%. These metal-metal bond cleavage reactions, as well as reactions that preserve the Os-Os multiple bond, are currently being explored. Full details will be reported in due course, along with complete details of the structural, spectroscopic, and electrochemical characterization of the triply bonded [Os₂X₈]²⁻ anions.

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Supplementary Material Available: Listing of atomic coordinates for the nongroup atoms and the rigid group atoms and anisotropic thermal parameters for the nongroup atoms (4 pages). Ordering information is given on any current masthead page.

(24) This appears to be an excellent general procedure for preparing complexes of the type [Os₂(μ-Cl)₃(PR₃)₆]X, although another procedure is available.²⁵

(25) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* 1961, 896.

An Example of Cyclometalation by Oxidative Addition: A Platinum(IV)-Tetramethylthiourea Complex Containing a Carbon-Metal σ Bond. Crystal Structure

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Thioamides and thioureas react with metals in high oxidation states not only as complexing agents but also as reductants.^{3,4,6}

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(1) GITER, Groupe Interuniversitaire Toulousain d'Etudes Radiocristallographiques.

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(3) Rasmussen, B. "Studies over Tiamidernes Konstitution"; Levin & Munksgaard: Copenhagen, 1922.

(4) (a) Devillanova, F. A.; Verani, G.; Battaglia, L. P.; Bonamarti Corradi, A. *Transition Met. Chem. (Weinheim, Ger.)* 1980, 5, 362-364. (b) Cristiani, F.; Devillanova, F. A.; Diaz, A.; Verani, G. *Inorg. Chim. Acta* 1981, 50, 251-255; 1983, 68, 213-221. (c) Castan, P. *Transition Met. Chem. (Weinheim, Ger.)* 1981, 6, 14-18.

(5) (a) Spofford, W. A., 3rd; Griffith, E. A. H.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* 1970, 533-534. (b) Griffith, E. A. H.; Spofford, W. A., 3rd; Amma, E. L. *Inorg. Chem.* 1978, 17, 1913-1923.

(6) (a) Kratochvil, B.; Zatko, D. A.; Markuszewski, R. *Anal. Chem.* 1966, 38, 770-778. (b) Kratochvil, B.; Zatko, D. A. *Ibid.* 1968, 40, 422-427. (c) Okaya, Y.; Knobler, C. N.; Pepinsky, R. Z. *Kristallogr.* 1959, 111, 385-387. (d) Spofford, W. A., 3rd; Amma, E. L. *J. Chem. Soc., Chem. Commun.* 1968, 405-408. (e) Spofford, W. A., 3rd; Amma, E. L. *Acta Crystallogr., Sect. B* 1970, B26, 1474-1476. (f) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* 1966, 88, 4270-4278. (g) Devillanova, F. A.; Isaia, F.; Verani, G. *J. Inorg. Nucl. Chem.* 1981, 43, 2749-2752.

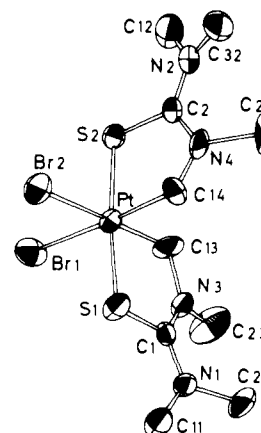


Figure 1. ORTEP illustration of the structure of the cyclometalated Pt(tmtu*)₂Br₂ complex.

Table I. Selected Geometric Features of the Complex

distance, Å		angle, deg	
Group I			
PtS(1)	2.313 (2)	Pt-S(1)-C(1)	98.9 (3)
S(1)C(1)	1.730 (7)	S(1)-C(1)-N(3)	116.6 (6)
C(1)N(3)	1.358 (10)	C(1)-N(3)-C(13)	122.1 (6)
N(3)C(13)	1.367 (10)	N(3)-C(13)-Pt	116.0 (5)
C(13)Pt	2.031 (7)	C(13)-Pt-S(1)	83.6 (2)
C(1)N(1)	1.326 (10)		
Group II			
PtS(2)	2.313 (2)	Pt-S(2)-C(2)	98.4 (3)
S(2)C(2)	1.727 (8)	S(2)-C(2)-N(4)	119.8 (6)
C(2)N(4)	1.334 (10)	C(2)-N(4)-C(14)	126.6 (8)
N(4)C(14)	1.475 (10)	N(4)-C(14)-Pt	113.3 (5)
C(14)Pt	2.045 (9)	C(14)-Pt-S(2)	86.2 (2)
C(2)N(2)	1.335 (10)		

To explain this reaction, it has been proposed that the thioamide reacts in its thiol form which is oxidized to a disulfide. N-substituted derivatives that do not permit thiol-thione tautomerism are able to complex metal ions in their higher oxidation state. For example, a copper (II) complex with tetramethylthiourea (tmtu) has been isolated⁵ while unsubstituted thioureas form only copper(I) complexes.

We report here the unusual behavior of tetramethylthiourea which reacts with the bridged dimer [Pt(tmtu)Br₂]₂ as an oxidizing agent to form Pt(tmtu*)₂Br₂, an octahedral Pt(IV) complex containing two metal-carbon σ bonds (tmtu* denotes the deprotonated form of tmtu).

This complex was prepared by adding tetramethylthiourea to aqueous K₂PtBr₄ in a 2/1 molar ratio. The product of the first step of this reaction has previously been identified as an orange dimer complex, [Pt(tmtu)Br₂]₂, in which the ligand acts as a bridge between the two platinum atoms.⁷ Adding more ligand redissolves this complex giving a pale yellow solution which yields, upon evaporation, pale yellow crystals suitable for X-ray study.

The compound was structurally characterized by a single-crystal X-ray diffraction study.⁸ An ORTEP illustration of this compound is presented in Figure 1 and selected bond lengths and angles are reported in Table I. As shown in this view of the molecule, the tmtu* ligands are bonded to the platinum atom through a sulfur

(7) (a) KuKushkin, Yu. N.; Sibirskaya, V. V.; Samuseva, V. N.; Strukov, V. V.; Pogoreva, V. G.; Mikhail'chenko, T. K. *Zh. Obshch. Zhim.* 1977, 47, 1402-1407. (b) Schafer, M.; Curran, C. *Inorg. Chem.* 1966, 5, 265-268.

(8) The compounds crystallizes in the monoclinic space group P2₁ with the following cell parameters: *a* = 10.405 (4) Å, *b* = 12.418 (1) Å, *c* = 14.141 (8) Å, β = 108.33 (4)°, *V* = 1734.4 Å³, *Z* = 2. The 3213 unique reflections are collected on an Enraf-Nonius CaD₄ diffractometer using Mo Kα radiation. The structure was solved using the Patterson heavy-atom method which revealed the position of the Pt atom. The remaining atoms were located by successive Fourier difference syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. *R*_F = 0.051 and *R*_{wF} = 0.064. Full details will be reported at a later date.

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.

(9) Pignedoli, A.; Peyronel, G. *Acta Crystallogr., Sect. B* 1978, B34, 1477-1482.

(10) Bachedi, F.; Zambonelli, L.; Marcotrigiano, G. *J. Cryst. Mol. Struct.* 1977, 7, 11-20.

(11) Martin, M. L.; Filleux-Blanchard, M. L.; Martin, G. J.; Webb, G. A. *Org. Magn. Reson.* 1980, 13, 396-402.

(12) Parshall, G. W.; Knoth, W. H.; Schunn, R. A. *J. Am. Chem. Soc.* 1969, 91, 4990-4995.

(13) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* 1968, 90, 909-913.

(14) Trofimenko, S. *Inorg. Chem.* 1973, 12, 1215-1221.

(15) Jones, E. C.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* 1974, 992-999.

(16) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* 1971, 3833-3842.

(17) Albinati, A.; Anklin, C. G.; Pregosin, P. S. *Inorg. Chim. Acta* 1984, 90, L37-L38.

(18) Alper, H. *J. Organomet. Chem.* 1973, 61, C62-C68.

(19) For a general review: Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* 1976, 18, 327-352 and references within.

(20) Parshall, G. W. *Acc. Chem. Res.* 1970, 3, 139-154.

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; K₂PtBr, 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

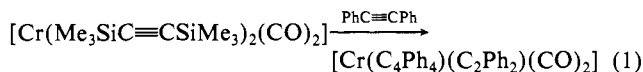
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We have recently provided evidence¹ that alkynes, like alkenes,² are sufficiently good π-acceptor ligands to form transition-metal complexes, analogous to carbonylmetalates, in which the metal has a negative oxidation state. It is also well established 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

† Fellow of the Alfred P. Sloan Foundation, 1982-1985.

(1) Maher, J. M.; Fox, J. R.; Foxman, B. M.; Cooper, N. J. *J. Am. Chem. Soc.* 1984, 106, 2347.

(2) Jonas, K. *Adv. Organomet. Chem.* 1981, 19, 97.

(3) (a) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* 1981, 103, 7713. (b) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* 1964, 86, 3261. (c) King, R. B. *Inorg. Chem.* 1968, 7, 1044. (d) Laine, R. M.; Moriarty, R. E.; Bau, R. *J. Am. Chem. Soc.* 1972, 94, 1402. (e) Kirillova, N. I.; Kolobova, N. E.; Gusev, A. I.; Antonova, A. B.; Struchkov, Yu. T.; Anisimov, K. N.; Khitrova, O. M. *J. Struct. Chem.* 1974, 15, 554. (f) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* 1975, 97, 1970. (g) Braterman, P. S.; Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* 1976, 241. (h) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* 1978, 100, 1318. (i) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* 1979, 101, 5094. (j) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* 1980, 19, 1997. (k) Davidson, J. L.; Manojlovic-Muir, L.; Muir, K. W.; Keith, A. N. *J. Chem. Soc., Chem. Commun.* 1980, 749. (l) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* 1981, 103, 1850. (m) Alt, H. G.; Hayen, H. I. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 1008. (n) Theopold, K.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 1010. (o) Capelle, B.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* 1983, 105, 4662. (p) Allen, S. R.; Green, M.; Moran, G.; Orpen, A. G.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* 1984, 441.

(4) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* 1980, 102, 1532. (b) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1980, 102, 3288.

(5) Dotz, K. H.; Mühlmeier, J. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 929. We have also developed a direct synthesis of this molecule from [Cr(CO)₃(NCEt)₃]: Wink, D. J.; Cooper, N. J., unpublished results.