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.

$$1 \xrightarrow[\text{THF}]{2[H_2NEt_2][S_2CNEt_2]} (Et_2NCS_2)(Et_2NCS)W(CO)(RCHS) \quad (2)$$
$$\textbf{4a}\ R = C_6H_5;\ 96\%$$
$$\textbf{4b},\ R = CH_3;\ 62\%$$

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.

---

[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_α) $= 56.4$ 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

---

[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.

0002-7863/86/1508-0311$01.50/0

we report the application of these principles to reductive coupling of carbon monoxide to form a new kind of CO-derived product, $Me_3SiOC{\equiv}COSiMe_3$, stabilized by coordination to tantalum(I).

The high-coordinate metal carbonyl chosen for reductive coupling was $[Ta(CO)_2(dmpe)_2Cl]$ (**1**), first prepared by Wreford,[8] where dmpe = 1,2-bis(dimethylphosphino)ethane. Crystals of **1** are isomorphous with those of $[Nb(CO)_2(dmpe)_2Cl]$, which has a C_{2v} capped trigonal-prismatic geometry with a short nonbonded contact of 2.27 Å between coordinated carbon atoms of the two CO ligands.[7] This geometry is known from EHMO calculations to be especially favorable for reductive coupling.[5] The metal center in **1** is quite electron-rich, as evidenced by the low CO stretching frequencies (1810, 1740 cm^{-1}) in its infrared spectrum. Compound **1** thus fulfills the steric, geometric, and electronic requirements found to be important in reductive coupling of isocyanides and seemed a likely system in which to observe reductive coupling of CO.

When 0.573 g (1 mmol) of **1** dissolved in THF were allowed to react with excess Mg dust (1.0 g, 41 mmol) activated by $HgCl_2$ (1.09 g, 4 mmol), in the presence of 0.432 g (1 mmol) of $(C_5Me_5)_2ZrCl_2$, the CO stretching bands gradually disappeared and new ones grew in at 1710, 1600, and 1525 cm^{-1}. These bands are attributed to the formation of η^2-CO bridges between tantalum and zirconium. Such "isocarbonyls" are well-known and many have been structurally characterized.[9] When conversion of yellow **1** to the red-brown intermediate **2** was complete, as judged by IR spectroscopy, the mixture was filtered and the filtrate treated with 0.254 mL (2 mmol) of Me_3SiCl at −78 °C. The solution slowly turned green upon warming to room temperature and stirring for 12 h. Removal of the solvent in vacuo, extraction of the residue with 40 mL of pentane, filtration, reduction of the volume to 4 mL, and cooling to −30 °C resulted in ~0.18 g (25% yield) of $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$ (**3**).[10]

The reductive coupling reaction was also observed when $(C_5R_5)_2TiCl_2$, R = H or Me, was used instead of the zirconium reagent, or I_2 was substituted for $HgCl_2$ to activate the magnesium. Typically isolated was a mixture of **3** and a second green crystalline product, tentatively identified by its spectroscopic properties[11] as $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2(SiMe_3)]$ (**4**). The ratio of **3** to **4** could be adjusted by varying the amount of Me_3SiCl added, the choice of Lewis acid, and the reagent used to activate Mg. Although isolated yields of this mixture were only 50%, ^{31}P NMR solution spectra showed no evidence for any species containing dmpe other than coupled ligand products.

In separate control experiments, it was found that neither activated Mg, $(C_5R_5)_2MCl_2$, nor Me_3SiCl react appreciably with **1**. Moreover, since $(C_5R_5)_2MCl_2$ compounds are known to be reduced by activated Mg,[12] it would appear that **2** is formed by reaction of **1** with a reduction product of $(C_5R_5)_2MCl_2$ and that **3** is derived from reaction of **2** with Me_3SiCl. Mechanistic studies are in progress.

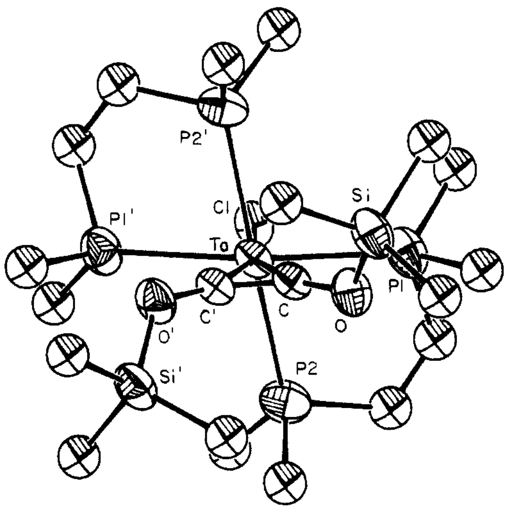

Figure 1. Structure of $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$ (**3**). For clarity, methyl and methylene carbon atoms are depicted as spheres with $B = 5.0$ Å^2. All other atoms show anisotropic thermal ellipsoids at 40% probability. Selected bond distances (Å) and angles (deg) are as follows: Ta–C, 2.079 (7); Ta–P1, 2.559 (2); Ta–P2, 2.546 (3); Ta–Cl, 2.727 (2); C–C′, 1.35 (1); Ta–C–O, 156.2 (5); C–O, 1.386 (8); O–C–C′, 132.6 (3); C–O–Si, 129.2 (5).

The molecular structure of **3** is shown in Figure 1.[13] Compound **3** is to our knowledge the first example of a structurally characterized molecule with an acetylene diether ligand.[14] The tantalum atom is coordinated in a pseudooctahedral manner in which the bis(trimethylsiloxy)ethyne and chloride ligands are trans to one another with the remaining sites occupied by two chelating dmpe ligands. These groups are tipped toward the sterically less demanding chloride atom such that the tantalum lies 0.45 Å toward the alkyne ligand side of the best plane through the four phosphorus atoms. A crystallographic twofold axis passes through the Ta—Cl bond and bisects the acetylenic $C{\equiv}C$ bond. The geometry (Figure 1) about the bis(trimethylsiloxy)ethyne ligand is comparable to that of other 4-electron donating alkyne complexes of tantalum.[15] Donation from two sets of alkyne π-orbitals, which provides an 18-electron configuration for the tantalum(I) atom, is also revealed by the ^{13}C NMR chemical shift of the alkyne carbon atoms (δ 212.5).[15b,16]

The infrared spectra of both **3** and **4** exhibit no bands in the CO stretching frequency region above 1600 cm^{-1}. A new band, characteristic of the coupled ligand, occurs at 1540 cm^{-1}. When a THF solution of a mixture of **3** and **4** is chromatographed on alumina, this band vanishes and a yellow solution containing only the IR bands of **1** is eluted. Presumably, basic oxygen sites on the alumina remove the trimethylsilyl groups from the coordinated bis(trimethylsiloxy)acetylene, which then uncouples with loss of two electrons to an as yet unidentified receptor. Precedence for such an uncoupling reaction is found in the dioxozirconacyclopenta-3,4-dienylidene diiron system studied by Bercaw.[1c] Removal of the $(C_5Me_5)_2Zr$ moiety as $(C_5Me_5)_2Zr(CO)_2$ under CO pressure uncoupled the ligand, regenerating the $(C_5H_5)_2Fe_2(CO)_4$ dimer. Analogous chemistry also occurs in the coupled isocyanide system. Treatment of $[Mo(t\text{-}BuHNC{\equiv}CNH\text{-}t\text{-}Bu)(CN\text{-}t\text{-}Bu)_4I]^+$ with 2 equiv of *n*-BuLi at −78 °C removes the protons of the coupled ligand and regenerates $[Mo(CN\text{-}t\text{-}Bu)_6I]^+$.[17]

In conclusion, we find that the factors promoting reductive coupling of isocyanides can be successfully applied to the reductive

---

(7) Bianconi, P.; Williams, I. D.; Lippard, S. J., unpublished results.

(8) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134. We prepared compound **1** by a modification[7] of the original procedure, which increased the yield from 48% to 90%.

(9) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

(10) Anal. Calcd for $C_{20}H_{50}ClO_2P_4Si_2Ta$ (**3**): C, 33.4; H, 7.01; Cl, 4.39. Found: C, 32.7; H, 6.63; Cl, 4.63. Spectroscopic data: IR (Nujol) 1540 cm^{-1}; ^{31}P NMR (36 MHz, THF, referenced to external H_3PO_4) δ 25.0 (s); ^1H NMR (250 MHz, C_6D_6) δ 1.51, 1.47 (s, PCH_3), 0.24 (s, $OSiCH_3$); ^{13}C NMR (67.9 MHz, C_6D_6) δ 2.20 (s, $OSiCH_3$), 18.38, 19.54 (s, br, PCH_3), 33.56 (t, J_{C-P} = 8 Hz, PCH_2), 212.5 (quint, J_{P-C} = 15 Hz, $\equiv COSiMe_3$).

(11) Spectroscopic properties (see ref 10) of **4**: IR (cm^{-1}) 1540; ^{31}P NMR δ 14.0 (s); ^1H NMR δ 1.78, 1.47 (s, PCH_3), 0.24 (s, $OSiCH_3$), 0.22 (s, $TaSiCH_3$); ^{13}C NMR δ 2.20 (s, $OSiCH_3$), 11.73 (br, m, $TaSiCH_3$), 24.50, 17.83 (s, br, PCH_3), 34.86 (t, J_{C-P} = 8 Hz, PCH_2), 211.6 (quint J_{C-P} = 15 Hz, $\equiv COSiMe_3$).

(12) Crystal data for **3**: $C_{20}H_{50}ClO_2P_4Si_2Ta$, $M_r = 719.1$, monoclinic, space group $I2/a$, $a = 16.399$ (2) Å, $b = 10.945$ (2) Å, $c = 19.209$ (5) Å, $\beta = 106.51$ (1)°, $V = 3305.8$ Å^3, $Z = 4$, $\rho_{calcd} = 1.445$ g cm^{-3}. The structure was solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares techniques. For 2479 unique, observed $[F_o \geqslant 2\sigma(F_o)]$ reflections measured by diffractometer and 138 variable parameters, the discrepancy index was $R_F = 0.046$.

(13) (a) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (b) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *101*, C24.

(14) A dimer of this ligand, $(Me_3SiOC)_4$, bound to the $Fe_2(CO)_6$ fragment, is reported in ref 3b.

(15) (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094. (b) Smith, G.; Schrock, R. R.; Churchill, M. C.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(16) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288. (b) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940.

(17) Warner S. W.; Lippard, S. J., unpublished results.

coupling of carbon monoxide. This discovery suggests that extension of the reaction chemistry to other ligand systems or to heteroligand coupling may be possible. The bis(trimethylsiloxy)ethyne ligand constitutes a new type of coordinated product derived from CO, and its formation here represents a novel synthetic route to an acetylene diether.[18] The generality of this reaction chemistry and the possibility of removing the alkyne moiety from the complex are currently being investigated.

Acknowledgment. This work was supported by a grant from the National Science Foundation (NSF-CHE-8542205). We also thank the M.I.T. Undergraduate Research Opportunities Program for partial financial support of M.P.E.

Supplementary Material Available: Atomic positional and thermal parameters for compound **3** (2 pages). Ordering information is given on any current masthead page.

---

(18) (a) Messeguer, A.; Serratosa, F. *Tetrahedron Lett.* **1973**, 2845. (b) Bou, A.; Pericàs, M. A.; Serratosa, F. *Tetrahedron* **1981**, *37*, 1441. (c) Pericàs, M. A.; Riera, A.; Serratosa, F. *Tetrahedron* **1982**, *38*, 1505.

Synthesis and X-ray Structure of $(C_5Me_5)_2Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$: A Complex with a Thorium–Platinum Bond

P. J. Hay, R. R. Ryan,* K. V. Salazar, D. A. Wrobleski, and A. P. Sattelberger*

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

Received July 5, 1985

In a recent paper,[1] we reported the synthesis of $Cp_2{*}Th(PPh_2)_2$[2] (**1**), and the preparation (eq 1) of $Cp_2{*}Th(\mu\text{-}PPh_2)_2Ni(CO)_2$ (**2**),

$$\underset{\mathbf{1}}{\mathrm{Cp_2{*}Th(PPh_2)_2}} + \mathrm{Ni(COD)_2} + 2\mathrm{CO} \xrightarrow[48\ \mathrm{h},\ 25\ ^\circ\mathrm{C}]{\mathrm{THF}} \underset{\mathbf{2}}{\mathrm{Cp_2{*}Th(\mu\text{-}PPh_2)_2Ni(CO)_2}} + 2\mathrm{COD} \quad (1)$$

the first phosphido-bridged heterobimetallic complex incorporating an actinide element. The X-ray structure of **2** revealed distorted tetrahedral environments about both metal centers, as well as two unexpected features: (1) acute Th-P-Ni angles which average 76.2 [4]° and (2) a short thorium-nickel separation of 3.206 (2) Å. These data led us to postulate the existence of a direct, albeit weak, thorium-nickel interaction, one that could be formulated as a donor-acceptor bond from Ni(0) to the electron-deficient Th(IV) center. Because bonding interactions between actinides (An) and transition metals (M) were unprecedented in discrete complexes,[3] we sought additional experimental evidence for donor-acceptor bonding in $Cp_2{*}An(\mu\text{-}PR_2)_2ML_n$ systems. Replacement of the $Ni(CO)_2$ fragment of **2** with an electron-rich transition-metal donor was a logical first step toward providing that evidence. Here we describe the synthesis, properties, and structure of a new thorium-platinum complex and provide some theoretical insight on the nature of the Th-Pt bond contained therein.

Toluene solutions of **1** react smoothly with 1 equiv of $Pt(COD)_2$[4] in the presence of trimethylphosphine (1-2 equiv) to provide

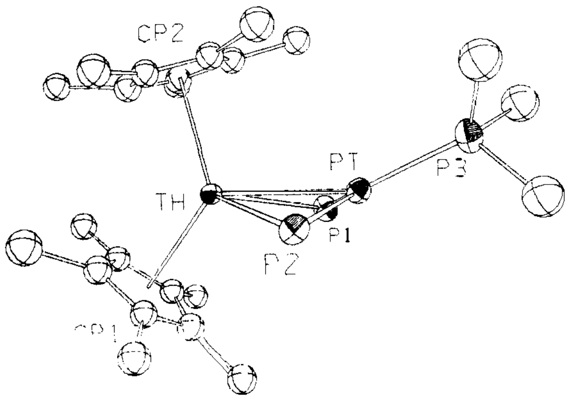

Figure 1. ORTEP II drawing of the $Cp_2{*}Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$ molecule. Hydrogen atoms and the phenyl groups on the $\mu\text{-}PPh_2$ ligands have been omitted for clarity (30% thermal ellipsoids).

red-brown, air-sensitive $Cp_2{*}Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$ (**3**) in ca. 50% isolated yield (eq 2).[5-7] The room temperature 200-MHz proton

$$\underset{\mathbf{1}}{\mathrm{Cp_2{*}Th(PPh_2)_2}} + \mathrm{Pt(COD)_2} + \mathrm{PMe_3} \xrightarrow[8\ \mathrm{h},\ 25\ ^\circ\mathrm{C}]{\mathrm{PhCH_3}} \underset{\mathbf{3}}{\mathrm{Cp_2{*}Th(\mu\text{-}PPh_2)_2Pt(PMe_3)}} + 2\mathrm{COD} \quad (2)$$

NMR spectrum of **3** in toluene-d_8 shows two methyl resonances at δ 1.86 (s, 30 H, Cp*) and 1.89 (s, 9 H, PMe_3). Cooling the sample to −90 °C had no significant effect on the appearance of the spectrum. The $^{31}P\{^1H\}$ NMR spectrum (81 MHz, 25 °C, toluene-d_8) consists of a doublet at δ +149.3 attributable to the $\mu\text{-}PPh_2$ groups and a triplet at δ −3.3 due to the terminal PMe_3 ligand. The spin system is AX_2 with $^2J_{pp'} = 7$ Hz. Each of the resonances is flanked by platinum-195 ($I = {}^1/_2$, 33.8% abundance) satellites. The $^{195}Pt{-}^{31}P$ coupling constants of 2459 Hz ($\mu\text{-}PPh_2$) and 2556 Hz (PMe_3) are much lower than the values of 4438 and 4188 Hz observed in the $^{31}P\{^1H\}$ NMR spectra of $Pt(PPh_3)_3$[8] and $Pt(PEt_3)_3$,[9] respectively, and are taken as an indication of four-coordinate platinum(0).[10]

An X-ray diffraction study of **3** revealed that the molecule crystallizes in the monoclinic space group $P2_1/n$ with $a = 16.394$ (3) Å, $b = 13.269$ (5) Å, $c = 24.319$ (4) Å, $\beta = 105.41$ (1)°, $V = 5100$ Å^3, and ρ(calcd) = 1.49 g cm^{-3} for $Z = 4$.[11] Solution of the structure by direct methods and Fourier techniques was followed by full-matrix least-squares refinements[11] which converged to an unweighted R value of 0.056 (Figure 1).

The most salient feature of the present structure is the Th-Pt distance of 2.984 (1) Å. An early estimate of the covalent single bond radius of Pt(0), viz., 1.31 Å,[12] has been revised to 1.38 Å by Otsuka and co-workers.[13] The latter value is consistent with the 2.77-Å separation in platinum metal,[14] the 2.765 (1)-Å Pt-Pt

---

(1) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501.

(2) Abbreviations used in the text: Cp* = $\eta^5\text{-}C_5(CH_3)_5$, Ph = phenyl, R = alkyl or aryl, COD = 1,5-cyclooctadiene, dmpe = 1,2-bis(dimethylphosphino)ethane, Cy = cyclohexyl, Et = ethyl.

(3) (a) Actinide-transition-metal bonding interactions have been established in several alloys.[3b,c] The complex $U[Mn(CO)_5]_4$[3d] may contain U-Mn bonds but this has not been demonstrated crystallographically. (b) Thomson, J. R. *Acta Crystallogr.* **1962**, *15*, 1308. (c) Brown, A. *Acta Crystallogr.* **1961**, *14*, 860. (d) Bennett, R. L.; Bruce, M. I.; Stone, F. G. A. *J. Organomet. Chem.* **1971**, *26*, 355.

(4) Spencer, J. L., *Inorg. Synth.* **1979**, *19*, 213.

(5) No $Cp_2{*}Th(\mu\text{-}PPh_2)_2Pt(PMe_3)_2$ was isolated from reaction mixtures containing excess PMe_3. In addition, **3** does not exchange with free PMe_3 in toluene solution at 25 °C on the phosphorus NMR time scale.

(6) Anal. Calcd for $C_{47}H_{59}P_3PtTh$: C, 49.34; H, 5.20; P, 8.12. Found: C, 49.95; H, 5.26; P, 7.31.

(7) Similar $Cp_2M(\mu\text{-}PR_2)_2Pt(PR_3')$ complexes (M = Zn, Hf; R = Ph, Cy, Et; R′ = Me, Ph, Cy) have been prepared by Baker using this route. Baker, R. T., personal communication.

(8) Leu, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

(9) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776.

(10) (a) $^1J_{\text{Pt-P}}$ values in parentheses. Compare $Pt(PPh_3)_3$ (4438 Hz) with $Pt(PPh_3)_3(CO)$ (3537 Hz) and $Pt(PPh_3)_2(CO)_2$ (3232 Hz) and $Pt(PEt_3)_3$ (4188 Hz) with $Pt(PEt_3)_4$ (3723 Hz). (b) The $Cp_2M(\mu\text{-}Pr_2)_2Pt(PR'_3)$ complexes of Baker,[7] which contain Zr- and Hf-Pt single bonds also exhibit characteristically low $J_{\text{Pt-PR}_2}$ (2200-2733 Hz) and $J_{\text{Pt-PR}_3}$ (3700-3987 Hz) coupling constants.

(11) Crystal data are presented as supplementary material.

(12) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(13) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(14) Wycoff, R. W. G. "Crystal Structures"; Wiley: New York, 1977; Vol. 1 and references therein.

0002-7863/86/1508-0313$01.50/0