biological tests and Drs. Murray Munro and John Blunt for providing data on mycalamide A prior to publication and helpful comments on the manuscript.

Supplementary Material Available: Relative configuration of onnamide A (**1**) (1 page). Ordering information is given on any current masthead page.

Synthesis and Physical Properties of a Dinuclear Tantalum–Cobalt Radical with Spin Localized at One Metal Center

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We wish to report the synthesis, physical characterization, and redox properties of $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$, a heterodinuclear organometallic radical species in which the unpaired electron is localized at one metal center.

Expecting to generate a diamagnetic $M(\mu\text{-}CH_2)M'$ adduct analogous to those that have been obtained previously,[1,2] we allowed the methylidene complex $Cp_2Ta(CH_2)CH_3$ (**1**)[3] to react with $CpCo(C_2H_4)_2$[4] (**2**) in C_6D_6 at 25 °C. However, when the reaction was monitored by ^1H NMR spectrometry, the reactants were seen to disappear over the course of 2.5 h, and resonances at δ 5.25 and 4.48, assignable to C_2H_4 and H_2, grew in along with a single broad resonance at δ 3.1. Orange X-ray quality crystals of an analytically pure product were isolated directly from the reaction solution in 64% yield. Elemental and mass spectrometric analyses were consistent with the formula $C_{17}H_{19}CoTa$ for this material and led to the suggestion that it has structure **3** shown in Scheme I.[5]

In order to confirm this supposition, a single-crystal X-ray diffraction study was undertaken; an ORTEP diagram of the structure of the complex is shown in Scheme I.[6] Crystals of **3** exist in space group $P2_12_12_1$. Both metal centers and the μ-methylene carbons lie in a plane which reflects the two equivalent tantalum cyclopentadienyl rings. This plane and the plane containing the metal centers and the centroids of all three cyclopentadienyl rings are almost exactly perpendicular (dihedral angle = 89.9°). The Ta–Co distance is 2.708 Å. The two $\mu\text{-}CH_2$–Ta distances of 2.11 and 2.13 Å are slightly shorter but consistent with those observed in other heteronuclear μ-methylene structures of tantalum (2.14–2.16 Å).[3] These distances fall roughly midway between those characteristic of a tantalum–carbon single bond (ca. 2.25 Å) and a tantalum–carbon double bond (ca. 2.03 Å).[7] The $\mu\text{-}CH_2$–Co distances of 1.98 and 1.97 Å are longer than those observed in homonuclear examples of μ-methylene cobalt complexes (1.91–1.92 Å).[8]

The ill-defined ^1H NMR spectrum of **3** and electron-counting formalisms (33 valence electrons) suggest that the molecule is paramagnetic. Magnetic susceptibility studies of **3** were carried out with a SHE Squid magnetometer, at 40 kG, over the temperature range 5–262 K. Curie–Wiess behavior was observed, and an effective magnetic moment of 1.91 μ_B was calculated from the data, indicating the presence of one unpaired electron.[9]

Electrochemical analysis indicates that **3** can be both oxidized and reduced reversibly in THF, with corresponding potentials of –0.38 and –2.44 V (relative to NHE).[10] The complete reversibility of the voltammogram and the relatively large difference in oxidation and reduction potentials of 2 V are indicative of the robust nature of **3** and suggest that the corresponding anion and cation salts might be stable. We have not yet been able to prepare the anion, but cationic salts can be readily generated. Thus, reaction of orange **3** with $Cp_2Fe^+BF_4^-$ in acetonitrile proceeded cleanly at 20 °C to give ferrocene and the purple diamagnetic complex $[Cp_2Ta(\mu\text{-}CH_2)_2Co(CH_3CN)Cp]^+BF_4^-\cdot CH_3CN$ (**4**) in 94% yield. Variable temperature NMR data indicate that the molecule is fluxional and are consistent with a process involving rapid dissociation and recoordination of the acetonitrile ligand above and below the plane of the $M\text{–}(CH_2)_2\text{–}M$ bridge. This process renders equivalent the two tantalum cyclopentadienyl signals, the two $\mu\text{-}CH_2$ hydrogens in each methylene unit, and the two CH_3CN ligands. Consistent with this mechanism, reaction of **4** with dative ligands PMe_3 and CO converts it rapidly to complexes **5a** and **5b**, respectively.

An important question concerning the electronic structure of **3** is the distribution of unpaired spin density about the two metal centers. The Ta/Co complex is an interesting heterodinuclear analogue of the dimeric cyclopentadienylcobalt "mixed valent"[11] radical anion $[CpCo(CO)]_2^-$, salts of which were prepared and studied several years ago.[12] The EPR spectrum of the dicobalt complex shows equivalent hyperfine coupling to the two cobalt atoms (^{59}Co, 100% abundant, $I = 7/2$), leading to a 15-line spectrum. Thus the unpaired electron is delocalized and is shared equally by the two metal centers. The EPR spectrum of **3** (note: ^{181}Ta, 99.99% abundant, $I = 7/2$) is quite different. At room temperature, the spectrum shows a single line with $g = 2.15$, having a line width of 143 G and no resolved hyperfine coupling. At low temperature the spectrum (obtained in a toluene glass at 8 K) shows an anisotropic signal with only an eight-line hyperfine coupling pattern (Figure 1). A simulated spectrum of an orthorhombic system with $I = 7/2$ allows assignment of the anisotropic g tensors and hyperfine coupling constants as indicated in the figure caption.[13]

The eight-line spectrum is thus consistent with isolation of the unpaired spin on one of the identical $I = 7/2$ metal centers, at least at low temperature. It is possible to write valence-bond structures (e.g., **3a** and **3b**; cf. Scheme I) that place the unpaired spin on either cobalt (a Co(II)/Ta(V) resonance form) or tantalum (a Co(III)/Ta(IV) form). Literature values for mononuclear

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(5) Anal. Calcd for $C_{17}H_{19}CoTa$: C, 44.08; H, 4.13. Found: C, 44.41; H, 4.26. HRMS(EI) 463.0298. Calcd for $C_{17}H_{19}CoTa$: 463.0298.

(6) The structure was determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-Ray Diffraction Facility (CHEXRAY). Crystal data: 1003 reflections; $R = 2.65\%$; space group $P2_12_12_1$; $a = 9.7333$ (9) Å, $b = 10.5263$ (13) Å, $c = 14.1131$ (17) Å; $\alpha = \beta = \gamma = 90.0°$; $Z = 4$, $d_{calcd} = 2.13$ g/cm^3. Other details of the structure determination are provided as Supplementary Material.

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(9) $\chi = C/(T - \theta)$; $C = 0.455$ K mol^{-1}; $\theta = -2.1$ K. μ_{eff} was calculated as $\mu_{eff} = 2.828\ (C)^{1/2} = 1.91\ \mu_B$. Although the value obtained for **3** is higher than that calculated for spin only contributions (μ_{eff}(spin only) $= g[S(S + 1)] = 1.73$), it is still consistent with values observed for systems with one unpaired electron. See: Figgis, B. N. *Introduction to Ligand Fields*; Interscience: New York, 1966.

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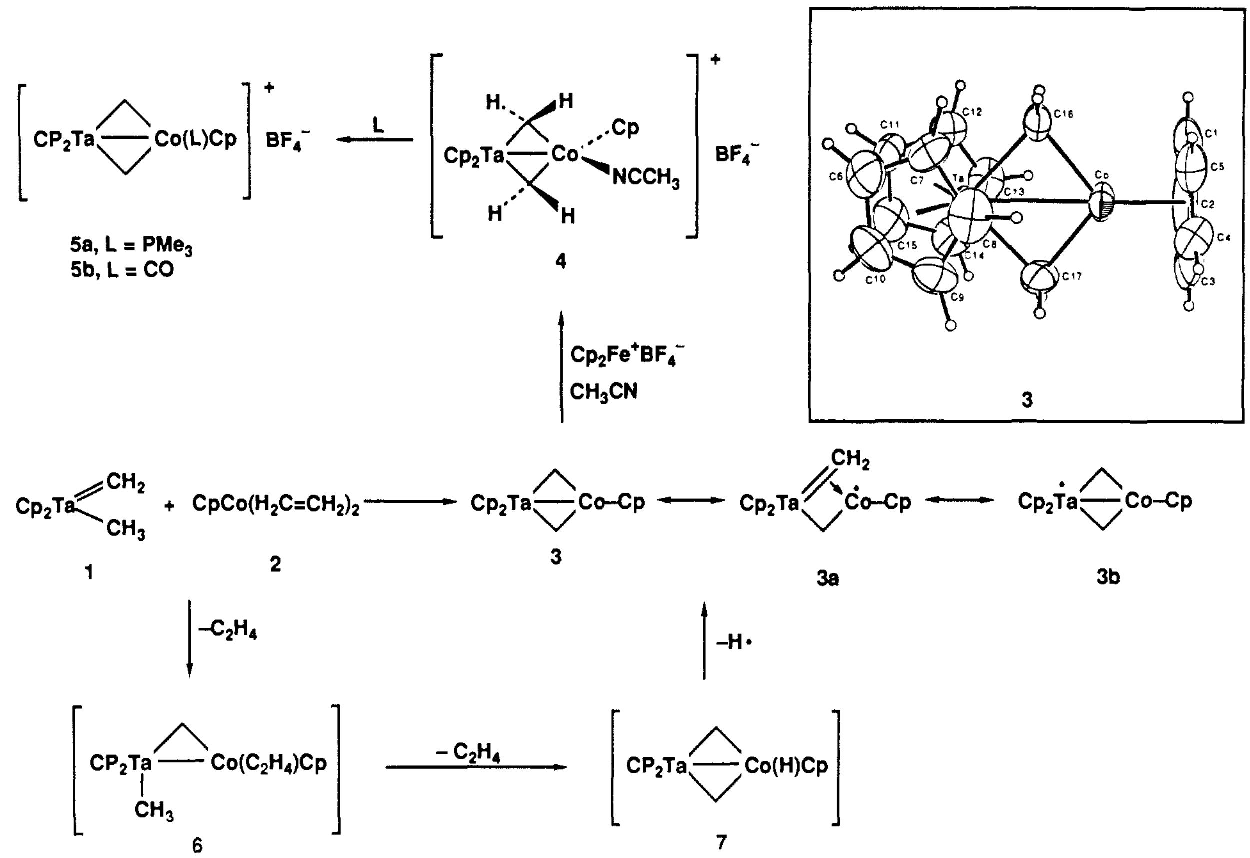
(13) The original developers of the fitting program, EPROW, were Drs. L. K. White and R. L. Belford, University of Illinois, Urbana, IL.

Scheme I



Ta(IV) complexes show ⟨g⟩ values in the range 1.94–2.006 and relatively large hyperfine coupling constants (60–140 × 10^{-4} cm^{-1}).[14] Co(II) complexes exhibit higher ⟨g⟩ values (2.08–2.167) and smaller hyperfine coupling constants (9–60 × 10^{-4} cm^{-1}).[15] The values of ⟨g⟩ = 2.143 and ⟨A⟩ = 26.7 × 10^{-4} cm^{-1} measured for **3** are clearly more consistent with spin localization at cobalt. The anisotropy of the spectrum of **3** also compares more favorably to model Co(II) than to Ta(IV) spectra.

We propose that **3** is formed by initial coordination of the Ta=CH_2 linkage to the cobalt center, giving intermediate **6** in the scheme, followed by loss of the second ethylene molecule and oxidative addition of a methyl C–H bond to the cobalt, leading to **7**. Most unusual, however, is the loss of hydrogen proposed in the last step, leading directly to **3**. The high stability of radical **3** must mean that the (so far unknown) hydride **7** has a very weak (and, presumably, kinetically very labile) M–H bond. Efforts are under way aimed at determining whether this hydride can be prepared and its chemistry investigated, in order to test these conclusions directly.

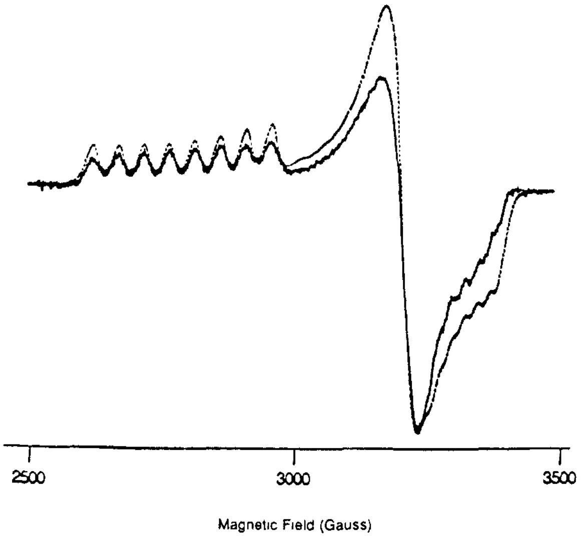


Figure 1. Observed (full line) and calculated (broken line) X-band EPR spectra of **1** in toluene at 8 K. The g and A (Co hyperfine coupling constants) values and σ (broadening parameters) used in the simulation are as follows: $g_x = 1.999$, $g_y = 2.065$, $g_z = 2.365$; $A_x = 22 \times 10^{-4}$ cm^{-1}, $A_y = 5 \times 10^{-4}$ cm^{-1}, $A_z = 53 \times 10^{-4}$ cm^{-1}; $\sigma_x = 5$ G, $\sigma_y = 35$ G; $\sigma_z = 18$ G.

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Supplementary Material Available: Spectroscopic and analytical data for **4**, **5a**, and **5b**, experimental details of the X-ray diffraction study of **3**, including crystal and data collection parameters, tables

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of positional parameters, general temperature factors, and intramolecular distances and angles (7 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

A Carbon–Carbon Bond Cleavage Reaction of Carbon Suboxide at a Metal Center. Synthesis and Structural Characterization of $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2-C(O)CPMePh_2\}$[†]

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Although the organic chemistry of carbon suboxide (O=C=C=C=O) has been studied in some detail since its discovery in 1906 by Otto Diels,[1] the inorganic reaction chemistry of C_3O_2 has only recently come under investigation.[2] We are currently exploring the use of C_3O_2 as a synthetic source of new ketene-type ligands in organometallic complexes. Our initial strategy has emphasized reactions of C_3O_2 with metal systems that are known to react cleanly with related heterocumulenes like carbon dioxide, isocyanates, ketenes, and carbodiimides. For example, the knowledge that low-valent hydrido complexes like $Re(H)(CO)_2(PPh_3)_3$ and $W(H)(CO)_2(NO)(PPh_3)_2$ undergo facile 1,2-insertion reactions with a wide range of heterocumulenes[3,4] led to the discovery of analogous insertion reactions between carbon suboxide and these metal hydrides that yield unprecedented formylketene ligands.[5] Recently, Mayer et al. described the reactions of O=C=O, RN=C=O, and RN=C=NR with $WCl_2(PMePh_2)_4$ (**1**).[6] These reactions proceed with elimination of $PMePh_2$ and formation of $W(O)Cl_2(CO)(PMePh_2)_2$, $W(NR)Cl_2(CO)(PMePh_2)_2$, and $W(NR)Cl_2(CNR)(PMePh_2)_2$, respectively. We were interested in investigating the reaction of **1** with carbon suboxide, anticipating the formation of a ketene-containing tungsten complex. Herein we report the results of this reaction and the structural characterization of the resulting ketenyl ylide product. This finding is an important one in our studies of the organometallic chemistry of C_3O_2 because it provides the first structural verification that a C–C bond of C_3O_2 can be cleaved at a metal center to give a carbonyl ligand and a coordinated ketenylidene equivalent.[2]

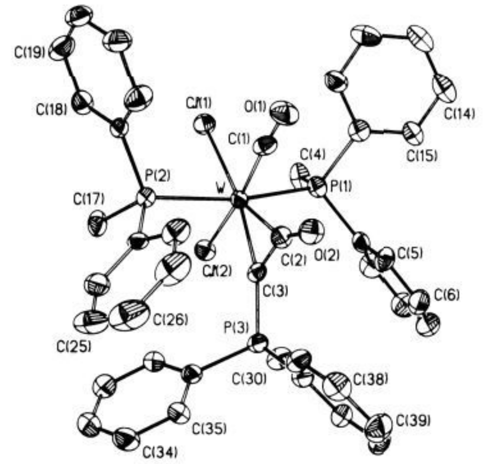
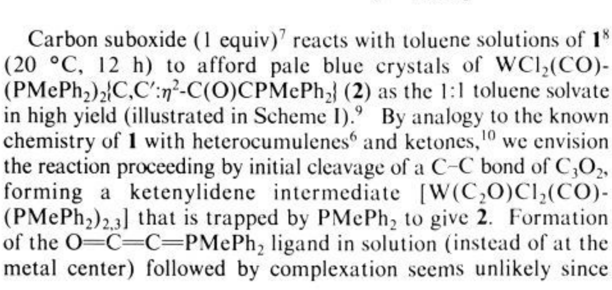


Figure 1. Molecular structure and atom labeling scheme for $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2-C(O)CPMePh_2\}$ (**2**) drawn with 40% thermal ellipsoids. W–Cl(1), 2.474 (2); W–Cl(2), 2.575 (2); W–P(1), 2.554 (2); W–P(2), 2.520 (2); W–C(1), 1.921 (10); W–C(2), 2.146 (9); W–C(3), 1.996 (8); C(1)–O(1), 1.175 (12); C(2)–O(2), 1.200 (11); C(2)–C(3), 1.368 (12); C(3)–P(3), 1.753 (8) Å; Cl(1)–W–Cl(2), 83.2 (1); Cl(1)–W–P(1), 84.6 (1); Cl(1)–W–P(2), 81.9 (1); Cl(1)–W–C(1), 85.8 (3); Cl(1)–W–C(2), 152.8 (2); Cl(1)–W–C(3), 168.0 (2); Cl(2)–W–P(1), 84.4 (1); Cl(2)–W–P(2), 90.8 (1); Cl(2)–W–C(1), 168.7 (2); Cl(2)–W–C(2), 124.0 (2); Cl(2)–W–C(3), 86.1 (2); P(1)–W–P(2), 166.2 (1); P(1)–W–C(1), 91.8 (2); P(1)–W–C(2), 96.7 (2); P(1)–W–C(3), 99.7 (2); P(2)–W–C(1), 90.5 (3); P(2)–W–C(2), 96.7 (2); P(2)–W–C(3), 92.9 (2); C(1)–W–C(2), 67.0 (3); C(1)–W–C(3), 105.1 (3); C(2)–W–C(3), 38.3 (3); W–C(1)–O(1), 176.2 (8); W–C(2)–O(2), 147.8 (6); W–C(2)–C(3), 64.9 (5); W–C(3)–P(3), 149.7 (5); W–C(3)–C(2), 76.8 (5); O(2)–C(2)–C(3), 147.2 (8); C(2)–C(3)–P(3), 133.0 (7) (deg).

Scheme I



Carbon suboxide (1 equiv)[7] reacts with toluene solutions of **1**[8] (20 °C, 12 h) to afford pale blue crystals of $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2-C(O)CPMePh_2\}$ (**2**) as the 1:1 toluene solvate in high yield (illustrated in Scheme I).[9] By analogy to the known chemistry of **1** with heterocumulenes[6] and ketones,[10] we envision the reaction proceeding by initial cleavage of a C–C bond of C_3O_2, forming a ketenylidene intermediate $[W(C_2O)Cl_2(CO)(PMePh_2)_{2,3}]$ that is trapped by $PMePh_2$ to give **2**. Formation of the $O=C=C=PMePh_2$ ligand in solution (instead of at the metal center) followed by complexation seems unlikely since

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[†] Dedicated to our colleague Professor Nien-Chu Yang on the occasion of his 60th birthday.

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(9) C_3O_2 (1.8 mmol) was condensed into a flask containing 1.69 g (1.6 mmol) of **1** suspended in 15 mL of toluene. The mixture was stirred for 12 h at ambient temperature and filtered, and the precipitate was washed with petroleum ether (15 mL) to give 1.32 g (81% yield) of $\mathbf{2}\cdot C_7H_8$. Recrystallization from CH_2Cl_2 gave solvent-free **2** as a blue, air-sensitive powder. For **2**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.94 (d, 3 H, $J_{PH} = 14.2$ Hz), 2.03 (t, 6 H, $J_{PH} = 4.0$ Hz), 7.0–8.0 (m, 30 H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, H_3PO_4 ref) δ 3.3 (s with W satellites, 2 P, $J_{PW} = 275$ Hz), 24.6 (s, 1 P); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 10.26 (d, $J_{PC} = 59.7$ Hz), 13.15 (t, $J_{PC} = 15.5$ Hz), 124–138 (m), 183.44 (dt, $^1J_{PC} = 56.5$, $^2J_{PC} = 7.0$ Hz), 211.94 (d, $J_{PC} = 12.1$ Hz); 219.6 (br s); IR (Fluorolube mull) $\nu_{CO} = 1910$ cm^{-1}, $\nu_{C=O} = 1673$ cm^{-1}. Anal. Calcd for $C_{42}H_{39}Cl_2O_2P_3W$: C, 54.63; H, 4.26; W, 19.91. Found: C, 54.29; H, 3.96; W, 20.08.

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