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 $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$[†]

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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]

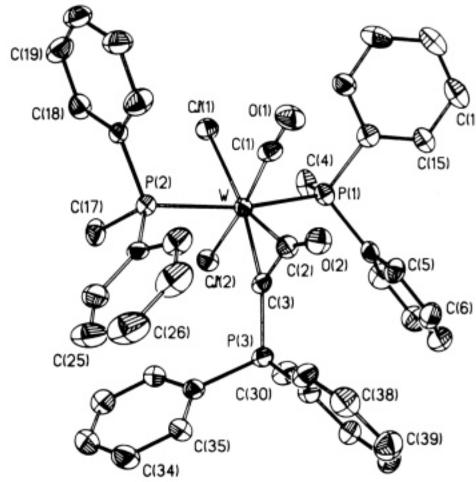
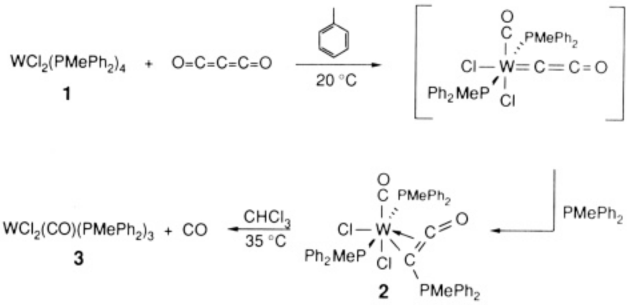


Figure 1. Molecular structure and atom labeling scheme for $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ (**2**) drawn with 40% thermal ellipsoids. W–Cl(1), 2.474 (2); W–Cl(2), 2.575 (2); W–P(1), 2.554 (2); W–P(2), 2.520 (2); W–C(1), 1.921 (10); W–C(2), 2.146 (9); W–C(3), 1.996 (8); C(1)–O(1), 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 $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ (**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 **2**·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) ν_{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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carbon suboxide and $PMePh_2$ do not react (1:1 stoichiometry) in the absence of the metal (^1H and ^{31}P NMR; IR). Attempts to intercept the ketenylidene by using phosphine traps have not been successful. Triphenylphosphoranylideneketene ($O{=}C{=}C{=}PPh_3$) is a stable molecule[11] and is known to form a moderately stable complex in $(CO)_5W\{\eta^1\text{-}C(CO)PPh_3\}$.[12] **2**, however, is the first example of a complex containing an η^2, 4-e donor ligand of this type and is closely related to known group 6 complexes containing η^2-ketenyl ligands, $M\{C,C'\text{:}\eta^2\text{-}C(O)CR\}$ (vide infra).[13]

The infrared spectrum of **2** exhibits two strong carbonyl absorptions that arise from the newly formed carbon monoxide ligand ($\nu(CO) = 1910$ cm^{-1}) and the η^2-ketenyl ylide ($\nu(C{=}O) = 1673$ cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum of **2** contains two resonances of relative intensity 2:1, with the larger having ^{183}W satellites and the smaller having none. Two distinct types of phosphorus moieties are also observed in the ^1H NMR spectrum: the methyl resonances for the $PMePh_2$ units appear as a doublet (δ 1.94, $J_{PH} = 14.2$ Hz) and a virtual triplet (δ 2.03, $J_{PH} = 4.0$ Hz) in a relative ratio of 1:2, characteristic of a phosphonium species (cf., $J_{PH} = 14.5$ Hz for $[PMe_2Ph_2^+]$) and a pair of *trans*-phosphine ligands, respectively.[9]

Diffraction quality crystals of unsolvated **2** were obtained by slow diffusion of ether into a saturated CH_2Cl_2 solution.[14] An ORTEP view of the structure of **2** with the atom numbering scheme is shown in Figure 1, along with salient intramolecular metrical parameters. The most striking feature of the structure is the novel η^2-diphenylmethylphosphoranylideneketene ligand. This $[\eta^2\text{-}C(O)CPMePh_2]$ fragment bears a close structural resemblance (in all relevant bond distances and angles) to η^2-ketenyl ligands in related tungsten(II) complexes (cf. $(Et_2NCS_2)(diphos)(CO)W\{C,C'\text{:}\eta^2\text{-}C(O)C\text{-}CH_2Ph\}$[13a] and $Cp(CO)(PMe_3)W\{C,C'\text{:}\eta^2\text{-}C(O)C\text{-tol}\}$[13d,e]). In comparison with $Ph_3P{=}C{=}C{=}O$,[11] the expected structural variations are observed on coordination of the phosphoranylideneketene in an η^2-fashion: (a) the P–C (1.648 (7) Å versus 1.753 (8) Å for **2**, $\Delta = 0.1$ Å) and the C–C (1.210 (10) Å versus 1.368 (12) Å for **2**, $\Delta = 0.16$ Å) bonds lengthen significantly on coordination and (b) the CCO angle deviates noticeably form linearity (175.6 (8)° versus 147.2 (8)° in **2**). The geometry of **2** is approximately octahedral if the $\eta^2\text{-}C(O)CPMePh_2$ ligand is considered as occupying one site in the coordination sphere. The new $\eta^2\text{-}C(O)CPMePh_2$ moiety is essentially planar. The largest deviation from the least-squares plane defined by W, Cl(1), Cl(2), C(1), C(2), C(3), O(1), O(2), and P(3) (i.e., all atoms of **2** except for P(1), P(2), and the Me and Ph groups) is 0.15 Å for Cl(2).

Like $(CO)_5W\{\eta^1\text{-}C(CO)PPh_3\}$,[12] at temperatures above 35 °C the phosphoranylideneketene moiety of **2** decomposes. As shown in Scheme I, the product of thermal decomposition of **2** in chloroform is the 16-e tungsten derivative $WCl_2(CO)(PMePh_2)_3$ (**3**) and carbon monoxide (determined by a Toepler measurement).[15] A spectroscopically (IR) detected dicarbonyl intermediate (probably $WCl_2(CO)_2(PMePh_2)_3$) is apparently involved in the transformation of **2** → **3**. We are currently attempting to ascertain the fate of the extruded "C atom" in this reaction.[16]

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Supplementary Material Available: Tables of atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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[14] Crystallographic data for **2**: $C_{42}H_{39}Cl_2O_2P_3W$, monoclinic, $P2_1/n$, $a = 11.400$ (4) Å, $b = 16.029$ (4) Å, $c = 21.569$ (9) Å, $\beta = 97.13$ (3)°, $V = 3910$ (2) Å^3, $Z = 4$, D(calcd) = 1.463 g·cm^{-3}, $\mu = 43.1$ cm^{-1}. Of 6588 reflections collected (Nicolet R3m diffractometer, 23 °C, Mo Kα, 2θ(max) = 50°), 6152 were independent ($R_{int} = 1.74\%$), and 4333 were considered observed. An empirical correction for absorption was applied to the data. The structure was solved by heavy-atom methods. The six phenyl rings were constrained to rigid, planar hexagons ($d_{C-C} = 1.395$ Å), and hydrogen atoms were treated as idealized, updated isotropic contributions. With all non-hydrogen atoms anisotropic, $R(F) = 4.1\%$, $R(wF) = 5.2\%$, GOF = 1.190, $\Delta/\sigma = 0.037$, $\Delta(\rho)$max = 1.84 e·Å^{-3} (1.02 Å from W), and $N_o/N_v = 11.4$. All computations used SHELXTL(5.1) software, Nicolet Corp., Madison, WI.

[15] A 0.51-g (0.6 mmol) sample of **2** was dissolved in $CHCl_3$ (25 mL) and maintained at 35 °C for 48 h. The volume of solution was reduced to 5 mL, and Et_2O was added to give a pink precipitate. Recrystallization from cold CH_2Cl_2 gave red-purple crystals of **3** (0.21 g, 51% yield). For **3**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (d, 3 H, $J_{PH} = 13.2$ Hz), 2.20 (t, 6 H, $J_{PH} = 3.6$ Hz), 6.9–7.6 (m, 30 H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, H_3PO_4 ref) δ 10.7 (d with W satellites, 2 P, $J_{PP} = 4$, $J_{PW} = 285$ Hz), −2.4 (t with W satellites, 1 P, $J_{PP} = 4$, $J_{PW} = 194$ Hz); $^{13}C\{^1H\}$ NMR (100.6-MHz, CD_2Cl_2) δ 12.3 (d, $J_{PC} = 61$ Hz), 14.7 (t, $J_{PC} = 14$ Hz), 124–140 (m), 219 (br m); IR (Fluorolube mull) $\nu_{CO} = 1903$ cm^{-1}. Anal. Calcd for $C_{40}H_{39}Cl_2OP_3W$: C, 54.38; H, 4.45. Found: C, 53.89; H, 4.17. A referee suggested **3** might actually be $WCl(CO)(CCl)PMePh_2)_3$; owing to its relative insolubility, our ^{13}C NMR data is not of sufficient quality to rigorously exclude this possibility, but the analytical data suggest otherwise.

[16] $(CO)_5W\{\eta^1\text{-}C(CO)PPh_3\}$ decomposes in the presence of cyclohexene to give $(CO)_5W(PPh_3)$ and 7,7′-spirobinorcarane (i.e., formal addition of "C" across the C–C double bonds of two cyclohexene molecules).[12]

Dercitin, a New Biologically Active Acridine Alkaloid from a Deep Water Marine Sponge, *Dercitus* sp.

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From our search for compounds from marine organisms with potential pharmacological utility, a violet pigment that exhibits antitumor, antiviral, and immunomodulatory properties in vitro[1] and antitumor properties in vivo was discovered. From spectroscopic analysis, including long-range ^1H–^{13}C correlation and natural abundance ^{13}C–^{13}C NMR experiments, the structure elucidation of this fused pentacyclic aromatic alkaloid, which we have designated dercitin (**1**), was achieved. This alkaloid represents a unique variation on fused-ring alkaloids previously found in marine organisms.[2]

Shipboard extraction (3:1 MeOH-toluene) and screening of fresh sponge material, collected by manned submersible at 160 m near Goulding Cay, Bahamas, showed significant in vitro ac-

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[1] Dercitin **1** had in vitro antitumor activity against P388 (IC_{50} 0.05 μg/ml) and human tumor cells (HCT-8, A-549, T47D, 1.0 μg/ml) and in vivo activity against P388 (T/C 170%, 5 mg/kg). Compound **1** had immunosuppressive activity in a murine derived, two-way mixed lymphocyte reaction assay (0% MLR, 0.01 μg/mL) and showed activity against Herpes simplex type 1 (10, ++ at 5 μg/well) and A-59 murine coronavirus (0, +++ at 1 μg/well) viral models (cytotoxicity: 16 = no viable cells, 8 = partial viability, 0 = no toxicity; antiviral activity: +++ = complete inhibition, + = partial inhibition, +/− = marginal inhibition, − = no protection).

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