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Carbonyl Displacement Reactions of $(C_5Me_5)TaCl_2(CO)_2(THF)$. Structures of $(C_5Me_5)TaCl_2(CO)_2(THF)$, $(C_5Me_5)TaCl_2(CO)(dmpe)$, and $(C_5Me_5)TaCl_2$(methyl acrylate)

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The synthesis and X-ray crystal structure of $(C_5Me_5)TaCl_2(CO)_2(THF)$ (1) have been studied. Complex 1 is prepared from the reduction of $(C_5Me_5)TaCl_4$ by $Al/HgCl_2$ under CO atmosphere and crystallizes in the orthorhombic space group $Pbn2_1$ with a = 9.152 (4) Å, b = 14.480 (7) Å, c = 13.738 (6) Å, V = 1821 (1) Å^3, and $Z = 4$. Least-squares refinement converged at $R = 0.039$ and $R_w = 0.036$ based on 1777 reflections with $I > 3\sigma(I)$. Compound 1 reacts with dmpe to yield the complex $(C_5Me_5)TaCl_2(CO)(dmpe)$ (3) in 80% yield. Compound 3 was characterized by a single-crystal X-ray diffraction analysis: space group $P2_1/n$; $Z = 4$; a = 9.463 (6) Å, b = 15.453 (7) Å, c = 14.713 (10) Å; V = 2121 (2) Å^3; $R = 0.055$ and $R_w = 0.053$ based on 2425 reflections with $I > 3\sigma(I)$. When allowed to react with methyl acrylate, compound 1 loses two COs to form $(C_5Me_5)TaCl_2$(methyl acrylate) (6) in 85% yield. Compound 6 was structurally chracterized: space group $Pbca$; $Z = 8$; a = 14.704 (4) Å, b = 15.694 (2) Å, c = 14.289 (4) Å; V = 3298 (1) Å^3; $R = 0.035$ and $R_w = 0.032$ based on 1412 reflections with $I > 3\sigma(I)$.

Introduction

Reduction of $CpMCl_4$ (M = Nb, Ta) with $Al/HgCl_2$ under CO atmosphere was first reported by Moorhouse et al.[1] The products were characterized as $CpM(CO)_3Cl_2$ and predicted to be useful starting materials for a variety of reactions, in particular, substitution reactions. Recently, as a part of our research into metal–metal multiple bonded complexes of the group V metals, we have structurally characterized the product and found it to be the chloro-bridged dicarbonyl dimer $[CpNbCl(CO)_2(\mu\text{-}Cl)]_2$ in the solid state.[2] In the course of developing its chemistry along the lines of CO displacement reactions, chloride replacement reactions, and reductive coupling,[3] we have encountered solubility problems with some of the products. When the Cp was replaced by Cp*, a monomeric complex, $(C_5Me_5)TaCl_2(CO)_2(THF)$ (1), was obtained from the reduction of Cp^*TaCl_4 with $Al/HgCl_2$ under CO. Here, we report the convenient synthesis, structure, and displacement reactions of 1 with π-acidic neutral ligands.

Experimental Section

The work described here involved the handling of very air- and/or moisture-sensitive materials. All operations were carried out under dinitrogen with use of standard Schlenk techniques or a drybox. Elemental analyses were performed by University of Michigan microanalytical service or by Galbraith Labs. Inc. (Knoxville, TN). Infrared measurements were made on a Nicolet 5DXB or Perkin-Elmer Model 1330 spectrometer. Mass spectra were obtained on a Finnigan Model 4021 GC–MS or VG 70-250s spectrometer. Nuclear magnetic resonance spectra were run on a Bruker AM-300 (operating at 300 MHz for ^1H and 75.5 MHz for ^{13}C). ^{31}P NMR spectra were obtained with a Bruker WM-360. The ^1H and ^{13}C spectra are referenced to TMS, and ^{31}P spectra were referenced to external 50% H_3PO_4. Tantalum pentachloride was purchased from Pressure Chemicals Co. and stored in the glovebox. Solvents were dried by Standard procedures and degassed prior to use. PMe_3 was prepared according to the literature procedure.[4] (Pentamethylcyclopentadienyl)tantalum tetrachloride was prepared by reaction of the tantalum pentachloride with $(C_5Me_5)Sn^nBu_3$, as described by Sanner[5] using the synthetic methodology modified by Bercaw et al.[6]

Synthesis of $(C_5Me_5)TaCl_2(CO)_2(THF)$ (1). A 500-mL side-arm flask was charged in the glovebox with 11 g (24 mmol) of yellow $(C_5Me_5)TaCl_4$, 0.9 g (33 mmol) of clean aluminum powder, a spatula tip of $HgCl_2$ (0.01–0.1 g, 0.04–0.4 mmol), and a stirring bar. The flask was transferred to the Schlenk line, and 200 mL of freshly distilled THF was added. Some of the solid dissolved to give a pale orange solution. The nitrogen branch of the Schlenk line was then connected to a tank of carbon monoxide.

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[1] Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. T. *J. Organomet. Chem.* **1980**, *186*, 237.

[2] Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940.

[3] (a) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644. (b) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M., submitted to *Organometallics*.

[4] Luetkens, M. L. Ph.D. Thesis, The University of Michigan, 1984.

[5] Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.

[6] Gibson, V. C.; Bercaw, J. E.; Bruton, W. J.; Sanner, R. D. *Organometallics* **1986**, *5*, 976.

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The flask was protected from the light with aluminum foil. The mixture was stirred under CO for 18 h. By that time, the color of the solution became orange-red. The remaining aluminum was filtered off through a Celite bed. The orange-red filtrate was concentrated in vacuo to ca. 50 mL. The orange product was collected by filtration, washed with five 10-mL portions of ether, and vacuum dried. The filtrate was concentrated further, and ether was added to obtain a second crop that was washed and dried in the same fashion. Overall yield: 10.5 g (85%) of bright orange microcrystalline product **1**: ^1H NMR (C_6D_6) δ 3.65 (m, 4 H, CH_2), 1.91, 1.74, 1.68, 1.60 (s, 15 H, C_5Me_5), 1.33 (m, 4 H, CH_2O); IR (THF, cm^{-1}) 2010 (st), 1918 (st); IR (Nujol, cm^{-1}) 2003 (st), 1902 (st). Anal. Calcd for $C_{16}H_{23}Cl_2O_3Ta$: C, 37.30; H, 4.50. Found: C, 37.04; H, 4.50.

Synthesis of (η^5-C_5Me_5)$TaCl_2$(ArC$\equiv$CAr) (2a,b). Two derivatives were prepared: Ar = C_6H_5 (**2a**) and Ar = *p*-MeC_6H_4 (**2b**). **1** (3 g, 5.82 mmol) was dissolved in 50 mL of THF. To this solution was added diphenylacetylene (1.2 g, 6.77 mmol) at room temperature. Gas evolution was observed, and stirring was continued overnight. The solution was concentrated and cooled to −8 °C. The product was allowed to crystallize. The orange product was collected by filtration, washed with cold hexane (2 × 10 mL), and dried in vacuo. The filtrate was concentrated further, and ca. 20 mL of hexane was added to obtain a second crop that was collected in the same fashion. Overall yield: 3.0 g (91%). **2b** was obtained by the same procedure with equally high yield. **2a**: ^1H NMR (CD_2Cl_2) δ 7.7–7.1 (m, m, m, 10 H, C_6H_5), 2.1 (s, 15 H, C_5Me_5). (These parameters are identical with those reported earlier.[7,8]) **2b**: ^1H NMR (C_6D_6) δ 7.75, 7.08 (d, d, pseudo A_2B_2, J = 8 Hz, 8 H, C_6H_4Me), 2.13 (s, 6 H, Ar*Me*), 1.86 (s, 15 H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 222.1 (Ar*CC*Ar), 139, 138.7, 130.7, 129.4 (C_6H_4Me), 120.9 (C_5Me_5), 21.3 ($ArCH_3$), 11.9 (C_5Me_5). Anal. Calcd for $C_{26}H_{29}Cl_2Ta$: C, 52.63; H, 4.93. Found: C, 52.24; H, 4.90.

Synthesis of (η^5-C_5Me_5)$TaCl_2$(CO)(dmpe) (3). In the glovebox, a 100-mL side-arm flask was loaded with 0.3 g (0.58 mmol) of **1** and 30 mL of THF. The flask was taken to the Schlenk line, and 0.15 mL (0.9 mmol) of bis(dimethylphosphino)ethane was added dropwise. The color of the solution initially turned brown and then green. The mixture was stirred until the CO bands of the starting material disappeared in the IR spectrum. Removal of solvent gave a green solid which was recrystallized from THF/hexane and dried under vacuum: yield 0.30 g (90%); ^1H NMR (C_6D_6) δ 1.9 (m, CH_2), 1.83 (s, 15 H, C_5Me_5), 1.66 (d, 3 H, J_{PH} = 9.62 Hz, CH_3), 1.50 (d, 3 H, J_{PH} = 10.5 Hz, CH_3), 0.98 (d, 3 H, J_{PH} = 8.08 Hz, CH_3), 0.74 (d, 3 H, J_{PH} = 7.11 Hz, CH_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 11.05 (d, $J_{PP'}$ = 9.3 Hz), 6.33 (d, $J_{PP'}$ = 9.4 Hz); IR (THF, cm^{-1}): 1840 (st); mass spectrum (EI, 70 eV), *m/e* 564 ($[Cp^*TaCl_2(CO)(DMPE)]^+$), 536 ($[Cp^*TaCl_2(DMPE)]^+$), 529 ($[Cp^*TaCl(CO)(DMPE)]^+$), 386 ($[Cp^*TaCl_2]^+$). Anal. Calcd for $C_{17}H_{31}Cl_2OP_2Ta$: C, 36.12; H, 5.53; Cl, 12.54; P, 10.96. Found: C, 35.90; H, 5.56; Cl,13.52; P, 9.33.

Synthesis of (C_5Me_5)$TaCl_2(CO)_2(PMe_3)$ (4). A 100-mL side-arm flask was loaded with 0.5 g (1 mmol) of **1** and 30 mL of THF. The flask was taken to the Schlenk line, and 0.3 mL (2.9 mmol) of trimethylphosphine was added dropwise at room temperature. The color of the solution changed slowly from brick red to purple. The mixture was stirred until the CO bands of the starting material disappeared in the IR spectrum (ca. 4 h). The THF was pumped off to give a purple solid. The product was dried in vacuo: yield 0.46 g (92%); ^1H NMR (C_6D_6) δ 1.75 (s, 15 H, C_5Me_5), 1.26 (d, J_{PH} = 9.68 Hz, 9 H, PMe_3). Anal. Calcd for $C_{15}H_{24}Cl_2O_2PTa$: C, 34.70; H, 4.66; Cl, 13.66. Found: C, 34.85; H, 4.80; Cl, 13.83.

Synthesis of (η^5-C_5Me_5)$TaCl_2$(CH_2=CHCOOMe) (6). To a stirred THF solution (30 mL) of **1** (0.5 g, 1 mmol) was added methyl acrylate (0.5 mL, 5.6 mmol) slowly at room temperature. The color of the solution changed from orange-red to brown and finally to purple after 20 min. The solution was stirred for a further hour after which the IR spectrum of reaction mixture showed complete disappearance of bands in the CO region. The solution was stripped to give a purple solid which was redissolved in ether (40 mL). The ether solution was filtered through a bed of Celite, and the filtrate was concentrated to give a crystalline product which was dried under vacuum: yield 0.40 g (87%); ^1H NMR (C_6D_6) δ 5.07 (d, d, J = 7.4 and 4.6 Hz, 1 H, C=C*H*), 3.40 (s, 3 H, OCH_3), 1.96 (s, 15 H, C_5Me_5), 1.26 (d, d, J = 7.4 and 8.4 Hz, 1 H, CH_2), 0.44 (d, d, J = 4.6 and 8.4 Hz, 1 H, CH_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 163.0 (CO_2C=C), 124.9 (C_5Me_5), 71.58 (*C*H), 66.79 (CH_2), 54.24 (OCH_3), 11.35 (C_5Me_5); ^{13}C NMR {gated ^1H} (C_6D_6) δ (a carbon resonance of CO_2 is not recorded) 124.9 (C_5Me_5), 71.58 (d, J_{CH} = 174 Hz, *C*H), 66.79 (t, J_{CH} = 148 Hz, CH_2), 54.24 (q, J_{CH} = 147 Hz, OCH_3), 11.35 (q, J_{CH} = 128 Hz, C_5Me_5); mass spectrum (EI, 70 eV), *m/e* 472 ($[Cp^*TaCl_2(CH_2CHCOOMe)]^+$), 437 ($[Cp^*TaCl(CH_2CHCOOMe)]^+$), 386 ($[Cp^*TaCl_2]^+$). Anal. Calcd for $C_{14}H_{21}Cl_2O_2Ta$: C, 35.54; H, 4.47. Found: C, 35.60; H, 4.45.

Crystallographic Analysis. The X-ray studies were carried out by using a Syntex $P2_1$ automatic diffractometer. Intensity data were obtained by using Mo Kα radiation (λ = 0.710 69 Å) with a graphite crystal monochromator. Intensity data were collected by the method of θ–2θ scans at a variable rate, dependent on peak intensity. Lattice parameters were obtained by least-squares analysis of 15 reflections scattered in reciprocal space, obtained from the automatic centering routine. Intensities of three standard reflections were monitored after every 50 data points. Background was measured before and after each peak; the background to scan time ratio was ca. 1.0. The solution and refinement of the structure were carried out on an IBM 3090/600E computer using the SHELX package that includes subroutines for direct methods, difference Fourier maps, least-squares refinements, and distance and angle calculations. The atomic scattering factors were taken from the ref 21. The data were corrected for Lorentz–polarization. The structures were solved by direct methods and refined by standard least-squares and difference Fourier methods. The function minimized by the least-squares program was $w(F_o - F_c)^2$ with the weights w, assigned as $1/(\sigma^2(F_o) + 10^{-4}F_o^2)$.

An orange crystal for X-ray diffraction was selected from the crop of crystals obtained by diffusion of ether into a solution of **1** in THF. A preliminary examination showed the crystal to be either a *Pbnm* (nonstandard setting of *Pnma*) or $Pbn2_1$ (nonstandard setting of $Pna2_1$). The structure was successfully solved by direct methods in space group $Pbn2_1$. An empirical absorption correction was applied to the intensities (μ = 62.24 cm^{-1}). The positions of all the non-hydrogens were obtained from subsequent difference Fourier and least-squares refinement. Refinement of positional and thermal parameters of all non-hydrogen atoms led to anisotropic convergence with R = 0.039 and R_w = 0.036. When the z coordinates were reversed in order to determine the correct enantiomeric form, convergence was reached with R = 0.052 and R_w = 0.050, which are significantly higher than those above.

Green crystals of **3** were obtained from THF/hexane at room temperature. A suitable crystal was sealed in a thin-walled capillary and mounted on a diffractometer. The structure was successfully solved by direct methods in space group $P2_1/n$ which was derived from systematically absent reflections. The positions of all non-hydrogen atoms were obtained from subsequent difference Fourier and least-squares refinements. Refinement of positional and thermal parameters of all non-hydrogen atoms led to isotropic convergence with R = 0.086 and R_w = 0.086. Anisotropic refinement yielded R = 0.058 and R_w = 0.056. Hydrogen atoms were then included in geometrically calculated positions with fixed isotropic temperature factors (0.07). Resulting R values are R = 0.053 and R_w = 0.055.

Purple crystals of **6** for X-ray diffraction were grown by slow evaporation of an ether solution under an atmosphere of purifed nitrogen. A plate-shaped crystal was sealed in a thin-walled capillary and mounted on a diffractometer. An empirical absorption correction was applied to the intensities (μ = 68.64 cm^{-1}). The structure was successfully solved by direct method in space group *Pbca* which was derived from systematically absent reflections. The positions of the non-hydrogen atoms were obtained from subsequent different Fourier and least-squares refinement. Refinement of positional and isotropic thermal parameters of all the non-hydrogen atoms led to convergence with R = 0.103 and R_w = 0.101. Anisotropic refinement yielded R = 0.037 and R_w

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(7) Schrock, R. R.; Smith, G.; Churchill, M. R.; Young, W. *Inorg. Chem.* **1981**, *20*, 387.

(8) Arnold, J.; Shina, D. N.; Tilley, T. D. *Organometallics* **1986**, *5*, 2037.

Table I. Crystallographic Data for $(C_5Me_5)TaCl_2(CO)_2(THF)$ (1), $(C_5Me_5)TaCl_2(CO)(DMPE)$ (3), and $(C_5Me_5)TaCl_2$(methyl acrylate) (6)

	1	3	6
formula	$C_{16}H_{23}Cl_2O_3Ta$	$C_{17}H_{31}Cl_2OP_2Ta$	$C_{14}H_{21}Cl_2O_2Ta$
mol wt	515.211	565.2	473.2
color	orange	green	purple
space group	$Pbn2_1$	$P2_1/n$	$Pbca$
a, b, c, Å	9.152 (4), 14.480 (7), 13.738 (6)	9.463 (6), 15.453 (7), 14.713 (10)	14.704 (4), 15.694 (2), 14.289 (4)
α, β, γ, deg	90, 90, 90	90, 99.62 (5), 90	90, 90, 90
cell vol, $Å^{-3}$	1821 (1)	2121 (2)	3298 (1)
Z	4	4	8
D(calcd), g/cm^{-3}	1.88	1.77	1.91
temp, °C	20	20	20
radiatn	Mo Kα	Mo Kα	Mo Kα
cryst dimens, mm	0.07 × 0.18 × 0.22 × 0.242	0.316 × 0.33 × 0.24	0.063 × 0.343 × 0.370
abs coeff, cm^{-1}	62.24	54.75	68.64
scan range (2θ/s)	2.5–12	2.5–12	2.5–12
bkgd/scan time	1.0	1.0	1.0
2θ, deg	45	45	45
unique data	2384	2793	2168
obsd data ($I > 3\sigma(I)$)	1777	2425	1412
largest metal residual, e/$Å^3$	1.97	2.18	0.96
largest nonmetal residual	0.87	0.60	0.49
R	0.039	0.055	0.035
R_w	0.036	0.053	0.032
goodness of fit	3.85	5.01	3.95

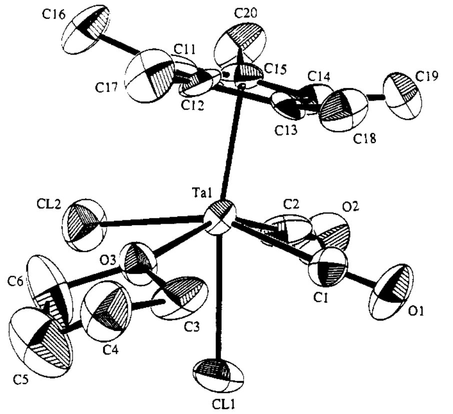
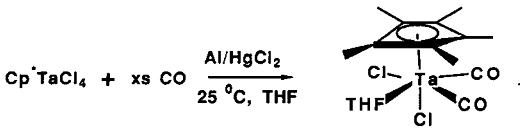


Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of $(C_5Me_5)TaCl_2(CO)_2(THF)$ (1) with the numbering scheme.

= 0.034. Hydrogen atoms were included in geometrically calculated positions with fixed isotropic temperature factors. Resulting R values are R = 0.035 and R_w = 0.032.

Results and Discussion

Reduction of Cp*$TaCl_4$ with Al/$HgCl_2$ in the presence of CO gave the Ta(III) complex 1 in a very high yield.



(1)

1

This complex was first reported by T. D. Tilley et al. as a product from the reaction of Cp*$TaCl_3(SiMe_3)$ with 50 psi of CO in 40% yield.[9] This complex reveals a somewhat complicated NMR spectrum in deuterated benzene. In the Cp* region, four broad peaks are observed at δ 1.91, 1.74, 1.68, and 1.60. The complex spectrum apparently results from dissociation of the THF and the formation of isomers and/or dimers in solution. In the IR spectrum, two strong CO bands of equal intensities were observed at ν = 2010 and 1918 cm^{-1} in THF. 1 decomposes in CH_2Cl_2 or toluene after a few days. The X-ray single-crystal structure determination (Figure 1) of the product 1 showed a monomeric structure with coordinated THF, which differs from the dicarbonyl dimer $[CpNbCl_2(CO)_2]_2$ obtained from $CpNbCl_4$ under the same reduction conditions. Steric hinderance of the Cp* ligand may inhibit dimerization. Final positional parameters for all non-hydrogen atoms are listed in Table II, and selected bond distances and angles are summarized in Table III. Complex 1 reveals a pseudooctahedral arrangement of the ligands with the Cp* ligand occupying one site. The two COs lie in a mutually cis positions, a chlorine is bonded in an axial position, and the THF is located at the cis position to C_5Me_5. The Ta1–C12 distance of 2.52 (2) Å and Ta1–C14 distance of 2.37 (2) Å indicate that the Cp* is tilted due to the trans effect of the CO ligands. Such ringl slip distortions have been seen in Cp*$TaCl_2$-

Table II. Fractional Atomic Coordinates for $(\eta^5-C_5Me_5)TaCl_2(CO)_2(THF)$ (1)

atoms	x	y	z	U, $Å^2$
Ta1	0.1199 (1)	0.3170 (0)	0.6898 (0)	0.031
Cl1	0.3728 (7)	0.2984 (4)	0.6247 (4)	0.062
Cl2	0.1000 (7)	0.4225 (4)	0.5468 (4)	0.063
O1	0.2888 (17)	0.1860 (13)	0.8399 (11)	0.070
O2	0.3091 (17)	0.4686 (11)	0.8027 (12)	0.063
O3	0.0807 (14)	0.2043 (9)	0.5757 (9)	0.044
C1	0.2273 (22)	0.2282 (16)	0.7832 (16)	0.043
C2	0.2419 (23)	0.4180 (15)	0.7623 (18)	0.044
C3	0.1129 (27)	0.1083 (14)	0.6006 (17)	0.063
C4	0.0567 (30)	0.0549 (19)	0.5130 (19)	0.079
C5	0.0993 (34)	0.1176 (23)	0.4347 (20)	0.104
C6	0.0736 (35)	0.2162 (18)	0.4705 (16)	0.085
C11	−0.1348 (20)	0.3702 (11)	0.6960 (36)	0.044
C12	−0.1427 (21)	0.2720 (14)	0.7185 (13)	0.042
C13	−0.0549 (21)	0.2560 (15)	0.8046 (14)	0.039
C14	−0.0033 (18)	0.3391 (11)	0.8399 (14)	0.032
C15	−0.0518 (21)	0.4087 (15)	0.7748 (16)	0.035
C16	−0.2303 (26)	0.4167 (17)	0.6252 (19)	0.063
C17	−0.2264 (21)	0.2009 (19)	0.6621 (15)	0.066
C18	−0.0628 (22)	0.1599 (14)	0.8577 (17)	0.052
C19	0.0589 (25)	0.3519 (15)	0.9400 (14)	0.050
C20	−0.0432 (24)	0.5167 (13)	0.7921 (17)	0.052

Table III. Bond Distances (Å) and Selected Bond Angles (deg) for $(\eta^5-C_5Me_5)TaCl_2(CO)_2(THF)$ (1)

Bond Distances			
Ta1–Cl1	2.496 (6)	Ta1–Cl2	2.496 (5)
Ta1–O3	2.292 (13)	Ta1–C1	2.065 (24)
Ta1–C2	2.092 (24)	Ta1–C11	2.457 (17)
Ta1–C12	2.521 (20)	Ta1–C13	2.413 (17)
Ta1–C14	2.372 (18)	Ta1–C15	2.366 (19)
O1–C1	1.139 (24)	O2–C2	1.107 (24)
O3–C3	1.461 (25)	O3–C6	1.457 (25)
C3–C4	1.520 (30)	C4–C5	1.461 (36)
C5–C6	1.527 (39)	C11–C12	1.457 (24)
C11–C15	1.435 (43)	C11–C16	1.470 (41)
C12–C13	1.448 (25)	C12–C17	1.499 (27)
C13–C14	1.380 (27)	C13–C18	1.573 (27)
C14–C15	1.418 (26)	C14–C19	1.500 (27)
C15–C20	1.583 (26)		
Bond Angles			
Cl1–Ta1–Cl2	81.5 (2)	Cl1–Ta1–O3	79.8 (4)
Cl2–Ta1–O3	83.4 (4)	Cl1–Ta1–C1	73.4 (6)
Cl2–Ta1–C1	154.8 (6)	O3–Ta1–C1	93.2 (6)
Cl1–Ta1–C2	75.6 (6)	Cl2–Ta1–C2	89.2 (6)
O3–Ta1–C2	155.1 (7)	C1–Ta1–C2	83.4 (8)

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[9] Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409.

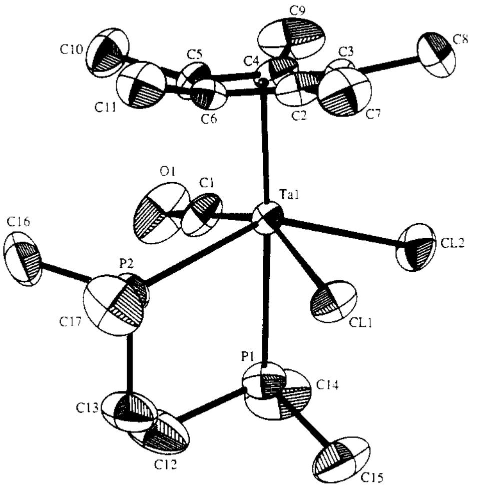
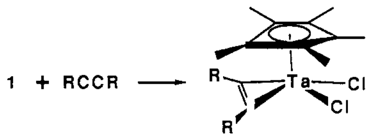


Figure 2. ORTEP plot (50% probability thermal ellipsoids) of the molecular structure of $(C_5Me_5)TaCl_2(CO)$ndmpe) (3) with the numbering scheme.

$(PMe_3)(CO)_2$[10] and $CpMo(CO)_2(\eta^2\text{-}O_2CO)^-$[11] and theoretically explained.[12]

Reaction of 1 with alkynes gave the known compounds $Cp^*TaCl_2(RC{\equiv}CR)$ in very high yields. The 16-electron complex **2a** has been prepared previously by R. R. Schrock[7] and T. D. Tilley.[8]



(2)

2a: R = Ph
2b: R = p-tolyl

Attempts to prepare a phosphine analogue by a similar route gave us the 18e complex $Cp^*TaCl_2(CO)$dmpe (3).

$$1 + \text{dmpe} \longrightarrow \text{Cp}^*\text{TaCl}_2\text{(CO)(dmpe)} \quad (3)$$

3

Compound 3 displays a molecular ion in the mass spectrum at *m/e* 564. A strong CO stretching frequency at 1840 cm^{-1} was observed which indicates a strong back-bonding between tantalum and carbon monoxide, compared to compound 1. The ^1H NMR spectrum displays four doublets at δ 0.74 (J_{PH} = 7.11 Hz), 0.98 (J_{PH} = 8.08 Hz), 1.50 (J_{PH} = 10.5 Hz), and 1.66 (J_{PH} = 9.62 Hz) which are assigned to the four chemically different methyl groups attached to the phosphorus. The $^{31}P\{^1H\}$ NMR spectrum showed two doublets at δ 11.05 ($J_{PP'}$ = 9.3 Hz) and 6.33 ($J_{PP'}$ = 9.4 Hz). Compound 3 was structurally characterized. Final positional parameters for all non-hydrogen atoms and selected bond distances and angles are reported in Tables IV and V, respectively. As shown in Figure 2, the molecule can be described as a distorted octahedron. Unlike $CpTaCl_2(PMe_2Ph)_2(CO)$,[13] one of the phosphorus atoms is in a trans position with respect to the Cp* in order to avoid the competition of back-bonding with CO. Similar structures have been reported in the complexes $CpNb(dppe)Cl_3$[14] and $CpMoCl_3(dppe)$,[15] where a phosphorus is bonded in the trans position to the cyclopentadiene ring.

Table IV. Fractional Atomic Coordinates for $(\eta^5\text{-}C_5Me_5)TaCl_2(CO)(dmpe)$ (3)

atoms	*x*	*y*	*z*	*U*, Å^2
Ta1	0.0445 (1)	0.2087 (0)	0.2614 (0)	0.022
Cl1	0.2833 (4)	0.2844 (3)	0.2942 (3)	0.041
Cl2	−0.0130 (5)	0.3312 (3)	0.1450 (3)	0.048
P1	0.1461 (4)	0.1641 (3)	0.1092 (3)	0.035
P2	0.2184 (5)	0.0796 (3)	0.3121 (3)	0.037
O1	−0.1659 (14)	0.0714 (8)	0.1498 (8)	0.064
C1	−0.0892 (17)	0.1227 (11)	0.1901 (10)	0.042
C2	0.0114 (16)	0.2796 (10)	0.4073 (10)	0.039
C3	−0.1010 (18)	0.3051 (9)	0.3382 (11)	0.044
C4	−0.1766 (16)	0.2309 (10)	0.3058 (10)	0.038
C5	−0.1152 (14)	0.1592 (9)	0.3580 (9)	0.027
C6	0.0066 (15)	0.1909 (9)	0.4194 (10)	0.030
C7	0.1161 (21)	0.3418 (12)	0.4639 (12)	0.061
C8	−0.1449 (24)	0.3980 (11)	0.3129 (15)	0.079
C9	−0.3259 (17)	0.2317 (15)	0.2466 (12)	0.064
C10	−0.1876 (20)	0.0736 (11)	0.3686 (12)	0.054
C11	0.0842 (19)	0.1431 (12)	0.5023 (10)	0.051
C12	0.2313 (22)	0.0572 (14)	0.1261 (12)	0.071
C13	0.3216 (21)	0.0539 (13)	0.2206 (12)	0.069
C14	0.0217 (20)	0.1501 (14)	0.0017 (11)	0.063
C15	0.2800 (23)	0.2332 (13)	0.0736 (13)	0.070
C16	0.1420 (22)	−0.0256 (10)	0.3334 (13)	0.061
C17	0.3740 (21)	0.0866 (14)	0.4061 (14)	0.068

Table V. Bond Distances (Å) and Selected Bond Angles (deg) for $(\eta^5\text{-}C_5Me_5)TaCl_2(CO)(dmpe)$ (3)

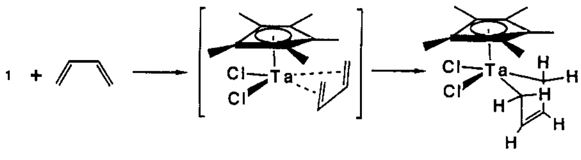
Bond Distances			
Ta1–Cl1	2.518 (4)	Ta1–Cl2	2.550 (4)
Ta1–P1	2.671 (04)	Ta1–P2	2.614 (4)
Ta1–C1	2.007 (17)	Ta1–C2	2.476 (15)
Ta1–C3	2.431 (15)	Ta1–C4	2.320 (15)
Ta1–C5	2.367 (13)	Ta1–C6	2.426 (14)
P1–C12	1.837 (20)	P1–C14	1.821 (16)
P1–C15	1.800 (18)	P2–C13	1.834 (17)
P2–C16	1.827 (18)	P2–C17	1.847 (18)
O1–C1	1.167 (18)	C2–C3	1.399 (22)
C2–C6	1.384 (20)	C2–C7	1.524 (22)
C3–C4	1.392 (22)	C3–C8	1.524 (22)
C4–C5	1.416 (20)	C4–C9	1.531 (21)
C5–C6	1.427 (19)	C5–C10	1.510 (21)
C6–C11	1.508 (20)	C12–C13	1.506 (25)
Bond Angles			
Cl1–Ta1–Cl2	82.4 (1)	Cl1–Ta1–P1	81.0 (1)
Cl2–Ta1–P1	72.2 (1)	Cl1–Ta1–P2	78.4 (1)
Cl2–Ta1–P2	144.3 (1)	P1–Ta1–P2	75.2 (1)
Cl1–Ta1–C1	151.1 (5)	Cl2–Ta1C1	95.5 (4)
P1–Ta1–C1	71.0 (4)	P2–Ta1–C1	87.4 (5)

A slight ring-slip distortion of the Cp* is also observed in this structure. Dmpe displaces only one CO from 1 while alkynes replace two COs. A similar result has been discussed by using EHMO theory in the previous paper.[3] On the other hand, PMe_3 displaces only THF to give a known dicarbonyl complex, 4, according to eq 4. This contrasts with the reaction of $[CpNbCl_2(CO)_2]_2$ with PMe_3, which gives a monocarbonyl complex, $CpNbCl_2(CO)(PMe_3)_2$.[3]

$$1 + \text{PMe}_3 \longrightarrow \text{Cp}^*\text{TaCl}_2\text{(CO)}_2\text{(PMe}_3\text{)} \quad (4)$$

4

Treatment of 1 with butadiene in THF affords the oxidized tantalum(V) complex Cp^*TaCl_2(butadiene) (5) in high yield. Compound 5 has been recently prepared by the reaction of Cp^*TaCl_4 with (2-butene-1,4-diyl)magnesium and structurally characterized.[16] When 1 was al-



(5)

5

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(10) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Organomet. Chem.* **1988**, *353*, C23.

(11) Curtis, M. D.; Han, K. R. *Inorg. Chem.* **1985**, *24*, 378.

(12) Chinn, J. W., Jr.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930.

(13) Burt, R. J.; Leigh, G. J.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 793.

(14) Prout, K.; Daran, J. C. *Acta Crystallogr.* **1979**, *B35*, 2882.

(15) Staerker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006.

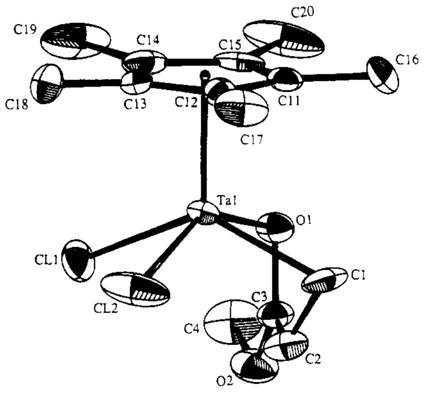
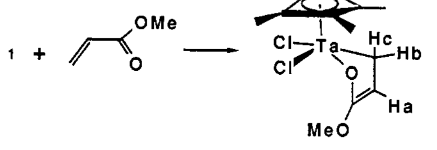


Figure 3. ORTEP plot (20% probability thermal ellipsoids) of the molecular structure of $(C_5Me_5)TaCl_2$(methyl acrylate) (6) with the numbering scheme.

lowed to react with methyl acrylate in the same fashion, the purple compound Cp^*TaCl_2(methyl acrylate) (6) was isolated.



6

(6)

Compound 6 displays a molecular ion in the mass spectrum at m/e 486. ^1H NMR revealed three doublets of doublets at δ 5.07, 1.26, and 0.44 which are assigned to an olefinic proton (H_a) and syn (Hb) and anti (H_c) protons with respect to H_a, respectively.[17] The $^{13}C-^1H$ coupling constants (J_{CH} = 148 Hz) of CH_2 from the methyl acrylate ligand indicates $sp^{2.5}$ hybridization of CH_2 on the basis of calculations using Newton's semiempirical equation.[18] The molecular structure of compound 6 is shown in Figure 3. Final positional parameters for all non-hydrogen atoms and selected bond distances and angles are reported in Table VI and Table VII, respectively. From the angle between the C1–C2–C3–O1 and C1–Ta–O1 planes (103.3°), the C1–C2 bond distance of 1.46 (2) Å, and the C2–C3 distance of 1.36 (2) Å, it is clear that the molecular has a bent metallacyclic structure (1-pentamethylcyclopentadienyl-1,1-dichloro-3-methoxy-1-tantala-2-oxacyclopent-3-ene) which resembles that found in the ketone adduct $CpTaCl_2$(2-methyl-2-penten-4-one), reported by W. A. Herrmann.[19]

Conclusions

A convenient and high-yield synthesis of the dicarbonyl complex $Cp^*TaCl_2(CO)_2THF$ allows the preparation of a variety of complexes of tantalum by simple and clean displacement reactions with no side products in the reaction mixture. Further reduction chemistry of these compounds to prepare and study metal–metal bonded complexes, especially multiply bonded complexes, is under investigation. Also, easily accessible alkyne and diolefin complexes allow us to study interesting transformations of organic moieties, e.g., to form metallocyclopentatrienes,[20] metallocyclopentene, and oxametallocycles. These studies may lead to new synthetic organic chemistry and a better understanding of mechanisms for the polymerization of alkynes by early-transition-metal complexes.

Table VI. Fractional Atomic Coordinates for (η^5-C_5Me_5)$TaCl_2$(methyl acrylate) (6)

atoms	x	y	z	U, Å^2
Ta1	0.5203 (0)	0.0924 (0)	0.2339 (0)	0.046
Cl1	0.4513 (2)	0.2309 (3)	0.2561 (3)	0.093
Cl2	0.4364 (3)	0.0487 (4)	0.3671 (3)	0.140
O1	0.5124 (6)	0.1192 (6)	0.0944 (6)	0.068
O2	0.3692 (6)	0.1570 (8)	0.0547 (8)	0.099
C1	0.4709 (8)	−0.0262 (9)	0.1707 (15)	0.102
C2	0.3981 (9)	0.0338 (12)	0.1482 (13)	0.087
C3	0.4252 (8)	0.1016 (11)	0.0955 (10)	0.069
C4	0.4077 (11)	0.2317 (13)	0.0124 (13)	0.118
C11	0.6677 (7)	0.257 (11)	0.2141 (11)	0.060
C12	0.6469 (8)	0.0231 (9)	0.3107 (11)	0.054
C13	0.6441 (7)	0.1037 (12)	0.3478 (12)	0.072
C14	0.6619 (8)	0.1630 (8)	0.2734 (17)	0.084
C15	0.6762 (7)	0.1124 (12)	0.1897 (12)	0.074
C16	0.6866 (10)	−0.0504 (13)	0.1539 (16)	0.136
C17	0.6380 (9)	−0.0596 (10)	0.3672 (13)	0.096
C18	0.6312 (10)	0.1333 (15)	0.4475 (13)	0.146
C19	0.6717 (10)	0.2572 (10)	0.2769 (23)	0.207
C20	0.7026 (10)	0.1431 (17)	0.0940 (16)	0.175

Table VII. Bond Distances (Å) and Selected Bond Angles (deg) for (η^5-C_5Me_5)$TaCl_2$(methyl acrylate) (6)

Bond Distances			
Ta1–Cl1	0.240 (4)	Ta1–Cl2	2.369 (4)
Ta1–O1	2.041 (8)	Ta1–C1	2.192 (14)
Ta1–C2	2.362 (15)	Ta1–C3	2.427 (14)
Ta1–C11	2.423 (11)	Ta1–C12	2.419 (12)
Ta1–C13	2.447 (13)	Ta1–C14	2.425 (12)
Ta1–C15	2.397 (11)	O1–C3	1.311 (13)
O2–C3	1.332 (16)	O2–C4	1.436 (18)
C1–C2	1.462 (19)	C2–C3	1.363 (20)
C11–C12	1.415 (19)	C11–C15	1.409 (21)
C11–C16	1.498 (21)	C12–C13	1.373 (19)
C12–C17	1.534 (19)	C13–C14	1.437 (22)
C13–C18	1.511 (21)	C14–C15	1.451 (22)
C14–C19	1.485 (20)	C15–C20	1.502 (22)
Bond Angles			
Cl1–Ta1–Cl2	86.3 (2)	Cl1–Ta1–O1	85.4 (3)
Cl2–Ta1–O1	144.5 (3)	Cl1–Ta1–C1	132.7 (4)
Cl2–Ta1–C1	85.0 (5)	O1–Ta1–C1	75.7 (6)
Ta1–O1–C3	90.0 (8)	Ta1–C1–C2	77.7 (9)

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Registry No. 1, 123931-14-6; **2a**, 75522-28-0; **2b**, 123857-64-7; 3, 123857-63-6; 4, 117120-25-9; 6, 123857-65-8; dmpe, 23936-60-9; $(C_5Me_5)TaCl_4$, 71414-47-6; PhCCPh, 501-65-5; p-$MeC_6H_4CCC_6H_4$-p-Me, 2789-88-0; PMe_3, 594-09-2; methyl acrylate, 96-33-3.

Supplementary Material Available: Tables of thermal parameters (Tables VIIIS–XS) and bond angles (Tables XIS–XIIIS) for 1, 3, and 6 (9 pages); listings of F_o vs F_c (Tables XIVS–XVIS) for 1, 3, and 6 (24 pages). Ordering information is given on any current masthead page.

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(16) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(17) (a) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuma, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388.

(18) Newton, M. D.; Shulman, T. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17.

(19) Guggolz, E.; Ziegler, M. L.; Biersack, H.; Herrman, W. A. *J. Organomet. Chem.* **1980**, *194*, 317.

(20) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668.

(21) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1974.