Three 18-Electron Tantalum(I) Compounds, $TaCl(CO)_2(dppe)_2$, $[TaCl(CO)_2(dppe)_2]_{2x}$, and $TaCl(CO)_4(dppe)$ (dppe = 1,2-Bis(diphenylphosphino)ethane), Which Exhibit Low Levels of Paramagnetism

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Reductive carbonylation of $TaCl_5$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) under the appropriate conditions results in the formation of $TaCl(CO)_2(dppe)_2$ (**1**), as the major product, and the possibly cyclic oligomer $[TaCl(CO)_2(dppe)_2]_{2x}$ (**2**, $2x \geq 4$) as a minor product. Carbonylation of **1** (1 atm) results in the rapid but reversible formation of $TaCl(CO)_4(dppe)$ (**3**). Solutions of all three compounds exhibit low levels of paramagnetism, possibly attributable to thermal population of low-lying triplet excited states. Crystal data for the toluene solvate of **1**, $C_{68}H_{64}ClO_2P_4Ta$: triclinic, $P\bar{1}$ (No. 2), $a = 13.937(12)$ Å, $b = 14.811(7)$ Å, $c = 14.929(9)$ Å, $\alpha = 102.30(5)°$, $\beta = 95.60(7)°$, $\gamma = 98.41(5)°$, $Z = 2$.

We have previously demonstrated the synthesis, via the reductive carbonylation of $TaCl_5$ in the presence of dppe (dppe = 1,2-bis(diphenylphosphino)ethane), of the novel 17-electron compound $Ta(CO)_4(dppe)$, the first simple group 5 heavy metal analogue of $V(CO)_6$ and its derivatives.[1] During the course of this research, the 18-electron, organotantalum compound $TaCl(CO)_2(dppe)_2$ (**1**)[2a] was occasionally formed as a byproduct during the formation of $Ta(CO)_4(dppe)$.[1b] In addition, the compounds $TaX(CO)_4(dppe)$ (X = Cl, Br, I)[2b,3] were formed as products of halogen abstraction reactions of $Ta(CO)_4(dppe)$ with organic halides RX,[1b] and since the tetracarbonyl compounds readily lose CO in the presence of free dppe, compound **1** again appeared in our lives. Seven-coordinated halotantalum(I) compounds of this type have been reasonably well-studied,[2b,4] crystal structure information for several being available, and there appeared initially to be no reason to pursue **1** further. However, **1** became interesting in its own right when we found that not only does it exhibit a low level of paramagnetism in solution, but also that an apparent oligomer of **1**, $[TaCl(CO)_2(dppe)_2]_{2x}$ (**2**, $2x \geq 4$), as well as $TaX(CO)_4(dppe)$ (**3**),[3] behave similarly. We have therefore optimized procedures for the syntheses of these three compounds, and discuss below their chemical and physical properties.

Experimental Section

Most experiments were carried out using standard Schlenk techniques under argon, which had been purified by passing through a heated column of BASF catalyst to remove traces of oxygen and through a column of molecular sieves to remove traces of water. Some manipulations of air- or moisture-sensitive solids were also accomplished in a Vacuum Atmospheres glovebox under a nitrogen atmosphere. All solvents were dried under nitrogen as follows: toluene, diethyl ether, benzene, and pentane over sodium and benzophenone; hexanes, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) over potassium and benzophenone; acetonitrile and dichloromethane over calcium hydride. All chemicals were purchased from Aldrich Chemicals, Strem, and BDH and were used as received. Carbon monoxide was passed through a column of molecular sieves; cylinders were not emptied below 500 psig since water was found to contaminate the last portion of the cylinder gas.

IR spectra were collected on Bruker IFS-85 or IFS-25 FT-IR spectrometers on samples prepared as solutions or as Nujol mulls. Raman spectra of finely-powdered samples in 5 mm glass tubes were obtained using a Bruker RFS-100 FT-Raman spectrometer.

Solution NMR spectra were recorded on Bruker AM-400 or ACF-200 FT spectrometers. Chemical shifts are reported in parts per million (δ), positive shifts being downfield from the reference. The chemical shift references used for solution spectra were tetramethylsilane (TMS) for ^1H NMR spectra and external H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. For ^1H NMR spectra, internal references in the form of TMS or the chemical shift of the residual proton of the deuterated solvent relative to TMS were used. Solid state NMR spectra were recorded on a Bruker CXP-200 FT spectrometer on solid samples tightly packed into a MAS sample probe. For solid state ^{13}C spectra, the reference used was adamantane (external). For solid state ^{31}P spectra, spectra were referenced to residual dppe (δ −12.0).

EPR spectra were recorded on a Varian E12 spectrometer equipped with a Bruker ER035M Gaussmeter and a Systron-Donner microwave frequency counter located at the National Research Council, Ottawa. Spectra were collected by Drs. K. F. Preston and P. Kaiser. The magnetic susceptibilities of solid samples were measured on a Johnson-Matthey magnetic susceptibility balance using finely-powdered solids packed into a glass sample tube to a depth of at least 1.5 cm. Magnetic susceptibilities in solution were determined using the Evans method,[5] cyclohexane and mesitylene being used as references for susceptibility shifts. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα graphite-monochromated X-ray irradiation.

$TaCl(CO)_2(dppe)_2$ (1). A solution of dppe (7.80 g, 19.6 mmol) in toluene (200 mL) was treated with $TaCl_5$ (3.50 g, 9.77 mmol) at 195 K, producing a yellow-orange slurry. A solution of sodium naphtha-

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Table 1. Crystallographic Data for **1**

chem form	$C_{68}H_{64}ClO_2P_4Ta$	vol, Å^3	2952(3)
fw, g mol^{-1}	1253.47	T, K	298(2)
space group	$P\bar{1}$ (No. 2)	λ, Å	0.710 69
a, Å	13.937(12)	D_{calc}, g cm^{-3}	1.410
b, Å	14.811(7)	μ, mm^{-1}	2.06
c, Å	14.929(9)	transm coeff	0.377−1.00
α, deg	102.30(5)	R^a	0.0560
β, deg	95.60(7)	R_w	0.1275
γ, deg	98.41(5)	Z	2

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths (Å)			
Ta−Cl	2.586(4)	Ta−P3	2.573(4)
Ta−C1	2.029(14)	Ta−P4	2.633(4)
Ta−C2	2.02(2)	C1−O2	1.153(14)
Ta−P1	2.632(4)	C2−O2	1.15(2)
Ta−P2	2.623(5)		

Bond Angles (deg)			
Cl−Ta−C1	130.8(4)	P1−Ta−P2	74.25(13)
Cl−Ta−C2	162.5(4)	P3−Ta−P4	71.94(13)
Cl−Ta−P1	96.04(12)	C1−Ta−C2	65.6(5)
Cl−Ta−P2	87.44(13)	Ta−C1−O1	176.0(12)
Cl−Ta−P3	76.84(12)	Ta−C2−O2	176.7(11)
Cl−Ta−P4	79.87(14)		

lenide, prepared from 10.0 g of naphthalene (78.0 mmol) and 0.9 g of sodium (39 mmol, cut into small pieces) in 150 mL of DME, was cooled and added to the $TaCl_5$−dppe slurry. The resulting brown mixture was warmed slowly to room temperature, where it was maintained for 30 min to 1 h. After cooling again to 195 K, CO was bubbled through the stirred mixture at 195 K for 4−6 h and then allowed to warm slowly to room temperature, under CO, overnight. The reaction mixture was then filtered through silica gel to remove a quantity of brown tar, resulting in dark red solution. The solution was pumped dry, and naphthalene was removed by sublimation.

The resulting solid was chromatographed on silica gel using hexanes, toluene, and, finally, CH_2Cl_2. Two red bands were eluted from the column and were isolated separately. The first was eluted with toluene and was found to consist of **1** (yield 3.2 g, 31%), as identified by the spectroscopic results below. The second band was eluted with CH_2Cl_2 and was identified as **2**, a possible oligomer, $[TaCl(CO)_2(dppe)_2]_{2x}$, of **1** (see below) (yield 260 mg, 2.5%). Compound **1** was recrystallized from THF/hexanes or toluene/hexanes. IR (THF or toluene): ν_{CO} 1833 (sharp, vs), 1762 cm^{-1} (m, br). IR (Nujol): ν_{CO} 1835 (s), 1756 cm^{-1} (m). Raman (powder): ν_{CO} 1835 (vs), 1761 cm^{-1} (m). ^{1}H NMR (toluene-d_8): δ 7.47 (br d, J = 18.3 Hz, 24H, phenyl), 6.93 (m, 8H, phenyl), 6.81 (m, 8H, phenyl), 2.52 (br s, 4H, CH_2), 1.78 (br s, 4H, CH_2). ^{1}H NMR (CD_2Cl_2): δ 7.31 (br s, 12H, phenyl), 7.23 (br s, 12H, phenyl), 7.18 (br s, 8H, phenyl), 7.00 (br s, 8H, phenyl), 2.59 (br s, 4H, CH_2), 1.97 (br s, 4H, CH_2). The resonances, especially of the CH_2 groups, are all broad, and there is little change in chemical shifts or line widths on decreasing the temperature to 197 K. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 47.5 (s); no change at 228 K. Solid state ^{31}P NMR: δ 57.3 (s), 44.0 (s), 33.8 (s). No EPR signal was observed for **1**, as a solid or in frozen benzene solution.

The compound is not sufficiently soluble in toluene-d_8 for the determination of the solution magnetic susceptibilities,[5] and samples were therefore prepared in CD_2Cl_2 to which cyclohexane and mesitylene had been added (5.0% (v/v) each). Measurements were made in the temperature range 183−298 K using a sample for which the concentration of **1** was 6.54×10^{-2} M at 298 K. The susceptibility shifts, $\Delta\nu$, were found to decrease from 9.7 Hz at 298 K to 6.7 Hz at 183 K. Compound **1** was found to be diamagnetic as a solid ($\chi_g = -3.48 \times 10^{-7}$ cm^3 g^{-1}).

Crystals of **1**, containing two molecules of toluene solvent per molecule of **1** and suitable for X-ray study, were obtained from a concentrated solution in toluene which was layered with hexanes. The solution was sealed tightly and maintained at −30 °C for 2 weeks. A platelike crystal of dimensions ~0.3 × ~0.3 × ~0.04 mm was mounted on a glass fiber with epoxy cement and sealed in an argon atmosphere in a thin glass capillary. Crystallographic data are collected in Table 1. The cell constants were obtained from least-squares refinement of 25 relections with 20° ≤ 2θ ≤ 25°. Intensity data were collected by $\omega-2\theta$ scans. Three standard reflections monitored throughout the data collection showed an ~10% decrease in their intensities, and a linear correction for this effect was applied on the basis of variation of standards' intensities.[6] The data were corrected for absorption using the program DIFABS,[7] and the structure was solved by heavy-atom methods (Patterson and Fourier maps) using the program XTAL 3.0.[6] Full-matrix least-squares refinement of F^2 data with anisotropic displacement parameters for all non-hydrogen atoms of **1** and of one of the toluene solvent molecules (C101−C107), and with the isotropic displacement parameters for all carbon atoms of a disordered toluene solvent molecule (C211−C237), was performed using the program SHELXL93;[8] the neutral atom scattering factors and anomalous dispersion corrections used are those from the *International Tables for Crystallography*.[9] The structure shows the presence of two toluene molecules per molecule of **1**, and they were refined as groups of rigid geometry with common isotropic displacement parameters (as ideal hexagons with ring C−C bonds of 1.390 Å and a methyl−phenyl bond of 1.51 Å; the latter bond was allowed to vary in the final cycles. One of the toluene molecules was found to be disordered and was refined in three positions (with atoms labeled C211−C217, C222−C227, and C231−C237 for three positions), for which the site occupancy factors were estimated to be 0.52, 0.25, and 0.23, respectively. Hydrogen atoms were placed in calculated positions (methyl group hydrogen atoms in two positions rotated by 60° with half of the occupancy of the methyl carbon). In the refinement, all hydrogen atoms were riding on the carbon atoms to which they are attached; their isotropic thermal displacement parameters were kept as $U_{iso}(H) = 1.2U_{eq}(C)$ (for aromatic H) or $U_{iso}(H) = 1.5U_{eq}(C)$ (for methyl H). The refinement converged at the final R (conventional, based on F) of 0.0560. Selected bond lengths and angles are listed in Table 2; fractional coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms, in Table 3. Tables of all bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, and hydrogen atom positional and thermal parameters for hydrogen atoms are available as Supporting Information. The geometrical analysis of the structure was done with the program SHELXL93. An ORTEP[10] drawing of **1** with the atom numbering scheme is shown in Figure 1.

$[TaCl(CO)_2(dppe)_2]_{2x}$ (2, 2x ≥ 4). During the synthesis of **1**, a second product **2** was obtained, as described above, and was recrystallized from THF/hexanes or toluene/hexanes. Anal. Calcd for $C_{54}H_{48}ClO_2P_4Ta$: C, 60.06; H, 4.52. Found: C, 61.64; H, 4.46. IR (toluene): ν_{CO} 1821 (sharp, vs), 1740 cm^{-1} (m, br). IR (Nujol): ν_{CO} 1819 (s), 1740 cm^{-1} (m). Raman (powder): ν_{CO} 1837 (s), 1747 cm^{-1} (m). ^{1}H NMR (CD_2Cl_2): δ 7.11−7.47 (m), 6.91 (m) (Ph), 5.28 (m, CH_2), 4.45 (m, CH_2), 2.79−2.89 (m), 2.69 (m), 2.40−2.60 (m) (CH_2), 2.00−2.20 (m, CH_2), 1.82 (m, CH_2), 0.51 (m, CH_2). In addition, ^{1}H NMR spectra were obtained in the temperature range 193−300 K. ^{1}H NMR in $CDCl_3$ at 193 K: δ 7.54 (m), 7.42 (m), 7.19−7.37 (m), 7.13 (m), 7.00 (m), 6.87 (m) (Ph), 5.11 (m), 4.28 (m), 2.90 (m), 2.79 (m), 2.50 (m), 2.44 (m), 2.10−2.40 (m), 2.08 (m), 1.90 (m), 1.81 (m), 1.67 (m), 0.35 (m) (all CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.4 (dd, J = 9.5, 77.1 Hz, 2P), 56.2 (dd, J = ~9, 82.7 Hz, 2P), 50.2 (dd, J = ~9, 78.9 Hz, 2P), 36.0 (dd, J = 11.0 Hz, 86.3 Hz, 2P). ^{31}P{^{1}H} NMR spectra of **2** were also obtained in CD_2Cl_2 over the temperature range 193−298 K. As the temperature decreased, the two central resonances converged, coincided at 218 K, and then diverged below 218 K. ^{31}P{^{1}H} NMR (CD_2Cl_2 at 193 K): δ 65.3 (dd), 55.1 (dd), 53.5 (dd),

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Table 3. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for Non-Hydrogen Atoms of $TaCl(CO)_2(dppe)_2$

atom	*x*	*y*	*z*	U_{eq}[a]
Ta	0.32645(5)	0.19886(4)	0.28316(4)	0.0548(3)
P1	0.2836(3)	0.0672(3)	0.3738(2)	0.0568(10)
P2	0.4936(3)	0.1503(3)	0.3330(2)	0.0569(11)
P3	0.3361(3)	0.3442(3)	0.2137(2)	0.0623(11)
P4	0.1562(3)	0.2559(3)	0.2864(3)	0.0601(11)
Cl	0.3675(3)	0.3369(3)	0.4274(2)	0.0658(11)
C1	0.3920(10)	0.1715(10)	0.1671(9)	0.063(4)
O1	0.4239(8)	0.1536(7)	0.0984(6)	0.077(3)
C2	0.2541(11)	0.0881(9)	0.1840(10)	0.058(4)
O2	0.2157(8)	0.0265(7)	0.1247(7)	0.084(3)
C3	0.3735(11)	0.0129(10)	0.3482(10)	0.072(5)
C4	0.4737(11)	0.0436(9)	0.3804(9)	0.061(4)
C5	0.2525(12)	0.4241(10)	0.2581(11)	0.080(5)
C6	0.1759(10)	0.3844(10)	0.3078(10)	0.069(4)
C10	0.1649(11)	0.0095(10)	0.3400(9)	0.060(4)
C11	0.0833(12)	0.0135(12)	0.3830(11)	0.071(4)
C12	−0.006(2)	−0.036(2)	0.3538(13)	0.101(6)
C13	−0.025(2)	−0.112(2)	0.2799(14)	0.116(8)
C14	0.058(2)	−0.1388(13)	0.2379(12)	0.108(7)
C15	0.1488(13)	−0.0856(11)	0.2655(10)	0.082(5)
C20	0.2996(10)	0.0868(11)	0.5015(9)	0.059(4)
C21	0.2603(10)	0.0207(10)	0.5473(11)	0.065(4)
C22	0.2710(12)	0.0370(14)	0.6399(12)	0.079(5)
C23	0.330(2)	0.116(2)	0.6911(11)	0.102(7)
C24	0.373(2)	0.1815(13)	0.6494(11)	0.098(6)
C25	0.3535(14)	0.1683(11)	0.5545(10)	0.086(6)
C30	0.5723(10)	0.1110(10)	0.2447(9)	0.056(4)
C31	0.6601(13)	0.1631(13)	0.2408(11)	0.094(6)
C32	0.7195(14)	0.134(2)	0.1768(13)	0.112(7)
C33	0.688(2)	0.052(2)	0.114(2)	0.125(8)
C34	0.600(2)	0.0003(13)	0.1132(10)	0.091(6)
C35	0.5405(11)	0.0277(11)	0.1803(10)	0.075(5)
C40	0.5861(11)	0.2303(11)	0.4239(9)	0.055(4)
C41	0.6404(11)	0.2036(11)	0.4862(11)	0.065(4)
C42	0.713(2)	0.266(2)	0.5496(11)	0.099(6)
C43	0.7273(14)	0.3606(14)	0.5472(13)	0.087(5)
C44	0.6703(14)	0.3863(14)	0.4822(13)	0.092(6)
C45	0.6001(11)	0.3236(13)	0.4204(10)	0.073(5)
C50	0.4559(12)	0.4189(10)	0.2367(10)	0.070(5)
C51	0.5251(14)	0.3931(12)	0.1794(12)	0.089(5)
C52	0.624(2)	0.4390(14)	0.201(2)	0.114(7)
C53	0.649(2)	0.515(2)	0.270(2)	0.102(6)
C54	0.584(2)	0.5421(11)	0.3284(12)	0.102(7)
C55	0.4870(14)	0.4922(11)	0.3087(10)	0.085(6)
C60	0.3033(13)	0.3321(12)	0.0890(10)	0.080(5)
C61	0.2527(12)	0.2459(12)	0.0344(11)	0.081(5)
C62	0.219(2)	0.241(2)	−0.0585(12)	0.109(7)
C63	0.242(2)	0.313(2)	−0.096(2)	0.152(10)
C64	0.292(2)	0.395(2)	−0.045(2)	0.176(13)
C65	0.325(2)	0.4011(14)	0.0468(13)	0.132(9)
C70	0.0680(10)	0.2111(12)	0.1836(9)	0.060(4)
C71	0.0422(13)	0.2666(13)	0.1265(13)	0.089(5)
C72	−0.026(2)	0.232(2)	0.0476(13)	0.116(7)
C73	−0.0641(13)	0.139(2)	0.0269(14)	0.096(6)
C74	−0.0413(13)	0.081(2)	0.081(2)	0.098(6)
C75	0.0275(12)	0.1182(12)	0.1602(12)	0.074(5)
C80	0.0798(13)	0.2400(10)	0.3803(10)	0.068(5)
C81	−0.0194(12)	0.2154(12)	0.3640(12)	0.084(5)
C82	−0.0712(14)	0.2063(14)	0.4378(14)	0.105(6)
C83	−0.027(2)	0.2212(14)	0.5226(14)	0.104(6)
C84	0.079(2)	0.2445(13)	0.5418(12)	0.100(6)
C85	0.1288(11)	0.2565(11)	0.4679(11)	0.076(5)

[a] The equivalent isotropic displacement parameter, U_{eq}, is calculated as $U_{eq} = (1/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

and 40.6. A ^{31}P COSY spectrum was obtained on a solution of **2** in $CDCl_3$. It was apparent from the spectrum that each phosphorus atom was coupled to each of the other three. Solid state ^{31}P NMR: δ 67 (s), 59 (s), 42 (s), 36 (s).

To measure the magnetic susceptibility in solution,[5] samples of **2** (25 mg) were prepared in 0.50 mL of CD_2Cl_2 to which cyclohexane and mesitylene had been added (5.0% (v/v) each). The susceptibilty shifts, $\Delta\nu$, were found to decrease from 3.7 Hz at 298 K to 2.8 Hz at 223 K; the resonances at 213 and 193 K were too broad to be resolved. The compound is diamagnetic as a solid ($\chi_g = -4.94 \times 10^{-7}$ cm^3 mol^{-1}). No EPR signal was observed, either on the solid or in frozen benzene solution.

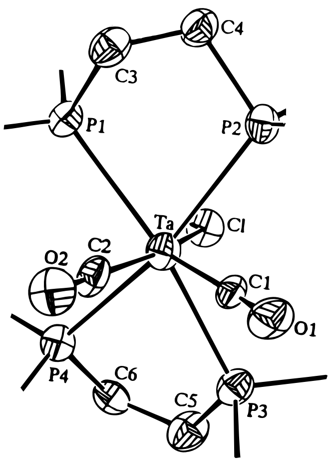

Figure 1. Molecular structure of **1** showing 30% probability displacement ellipsoids and the numbering scheme. Phenyl groups and hydrogen atoms are omitted for clarity.

$TaCl(CO)_4(dppe)$ (3). Carbon monoxide was bubbled through a solution of **1** in toluene for 5 min, at which point the carbonyl bands of the **1** had disappeared and a new set, attributable to $TaCl(CO)_4(dppe)$ (**3**), had appeared. IR (toluene): ν_{CO} 2025 (m), 1952 (w), 1904 (s), 1885 cm^{-1} (m). Lit.[3] (toluene): ν_{CO} 2023 (s), 1948 (m), 1900 (vs), 1883 cm^{-1} (ms). The reaction was found to be reversible. By replacing CO with argon, **1** was re-formed within 5 min. In addition, removing the solvent (under vacuum) from a solution containing **3** and free dppe also resulted in the formation of **1**. Compound **2** was found not to react with carbon monoxide; the infrared spectrum of **2** in toluene was unchanged after 1 h of CO bubbling.

The reaction of **1** with CO in toluene-d_8 was monitored by NMR spectroscopy. ^1H NMR of **3** (toluene-d_8): δ 7.63 (m, Ph), 7.35 (m, Ph), 6.80 (m, Ph), 2.90 (br m, 1H, CH_2), 2.73 (br m, 1H, CH_2), 1.70 (br m, 2H, CH_2). A similar sample of **1** was carbonylated in order to measure the magnetic susceptibility of **3** by the Evans method.[5] Thus, 25 mg of **1** was dissolved in 0.50 mL of CD_2Cl_2 (concentration = 0.0466 M at 298 K) containing cyclohexane and mesitylene (5.0% each), and, after a ^1H NMR spectrum was obtained, carbon monoxide was bubbled into the sample for 5 min. The sample was found to be paramagnetic after bubbling with CO ($\Delta\nu = 6.2$ Hz).

Results and Discussion

Synthesis and Characterization of $TaCl(CO)_2(dppe)_2$ (1). Although a variety of synthetic routes to compounds of the type $TaX(CO)_2(L_2)_2$ (X = halide, L_2 = bidentate ligand) have been reported, both direct and indirect,[4] the only previously reported synthesis of **1** involved the photolysis of $TaH(CO)_2(dppe)_2$ in THF in the presence of $(Et_4N)Cl$.[2a] This is not a convenient route to **1** since it requires first the synthesis of $TaH(CO)_4(dppe)$.[1b] However, since we have successfully synthesized $TaH(CO)_4(dppe)$ in a convenient, one-step reaction from $TaCl_5$,[1b] a similar approach was tried for the synthesis of **1**. In this procedure, a mixture of $TaCl_5$, dppe, and sodium naphthalenide was formed at −78 °C and then warmed to room temperature and stirred for 0.5−1 h. The reaction mixture was then recooled to −78 °C and stirred for several hours under 1 atm of CO. The mixture was allowed to warm to room temperature under CO, and the product, **1**, was obtained in 31% yield after workup as described in the Experimental Section. This method requires fewer steps than do many previously reported syntheses of compounds of this type,[4] and the yields (based on $TaCl_5$) are higher than those reported previously for **1**.[2a]

It was found that **1** is thermally quite stable, as solutions can be heated to 60 °C for periods of a few hours without decomposition. In addition, there was no change noted in the IR or ^{1}H NMR spectra of the solid material after several days at room temperature under nitrogen. Solid **1** is moderately air-stable, although extended exposure to humid air results in conversion to a white, non-carbonyl-containing material. Hydrolysis to a presumably similar white material on dissolution in solvents contaminated with trace amounts of water is rapid.

The IR (solution and solid) and Raman (solid) spectra of **1** all exhibit two carbonyl stretching bands at ~1830 and ~1760 cm^{-1}. The spectra are thus consistent with mutually *cis* CO ligands, as verified by the crystal structure (see below), and suggest that the same structure exists in the solid state and in solution. While the data compare well with IR data reported for the similar compounds TaX(CO)$_2$(dmpe)$_2$,[4a,e] TaI(CO)$_2$(dppe)$_2$[2b] and NbX(CO)$_2$(dppe)$_2$ (X = Cl, Br),[2b] it has previously been reported that the IR spectrum of **1** in THF solution exhibits only a single carbonyl band, at 1730 cm^{-1}.[2a] Our results, which are highly reproducible from one batch of **1** to another, prepared over several years and utilizing various routes, suggest that the earlier report is in error.

Resonances in the ^{1}H NMR spectrum of **1**, especially those of the CH$_2$ hydrogens, which exhibit no fine structure, are all broad in contrast to the corresponding resonances of TaH(CO)$_4$(dppe) and [Et$_4$N][Ta(CO)$_4$(dppe)], which are well-resolved.[1b] There is little variation in the spectrum of **1** on cooling to 193 K. In contrast, the solution ^{31}P{^{1}H} NMR spectrum of **1** exhibits a sharp singlet (δ 47.5 in CDCl$_3$), similar to TaH(CO)$_4$(dppe) (δ 43.9 in CD$_3$CN) and [Et$_4$N][Ta(CO)$_4$(dppe)] (δ 49.2 in CD$_3$CN). The solid state ^{31}P NMR spectrum exhibits resonances broadened presumably because of quadrupolar coupling to ^{181}Ta ($I = 7/2$).[11]

The two methylene resonances in the ^{1}H NMR spectrum of **1** occur at δ 2.52 and 1.78 in toluene-d_8, at δ 2.59 and 1.97 in CD$_2$Cl$_2$ and thus are separated by 0.74 and 0.62 ppm in the two solvents, respectively. Since these separations are too large (250−300 Hz at 400 MHz) to reflect spin−spin coupling to ^{31}P, the methylene hydrogens must exist in two environments, consistent with the crystal structure of **1** (see below). However, while the lower field resonances are only marginally lower than anticipated,[12] the large separation may imply the presence of small contact shifts.[13]

In order to definitely prove that the material used in these experiments was the previously-reported, 18-electron **1**, X-ray quality crystals were grown from toluene and the molecular structure was determined. The compound is monomeric and assumes a capped trigonal prismatic structure, with mutually *cis* CO ligands and the chlorine capping the P$_4$ face, as illustrated in idealized fashion in Figure 2A. An ORTEP structure (phenyl groups and hydrogen atoms omitted for clarity) showing the numbering scheme and 30% probability displacement ellipsoids is illustrated in Figure 1 and important bond lengths and angles are given in Table 2; the metal−ligand bond lengths all seem normal. The crystalline material also contains two molecules of toluene per one molecule of tantalum compound, one of them disordered.

The structure is, as anticipated, very similar to that of the niobium analogue, NbCl(CO)$_2$(dppe)$_2$,[14] and to those of TaI(CO)$_4$(dppe),[3] TaCl(CO)$_2$(depe)$_2$ (depe = 1,2-bis(diethylphosphino)ethane),[4e] and TaCl(CO)(CNR)(dmpe)$_2$ (R = Et, *t*-Bu).[4f]

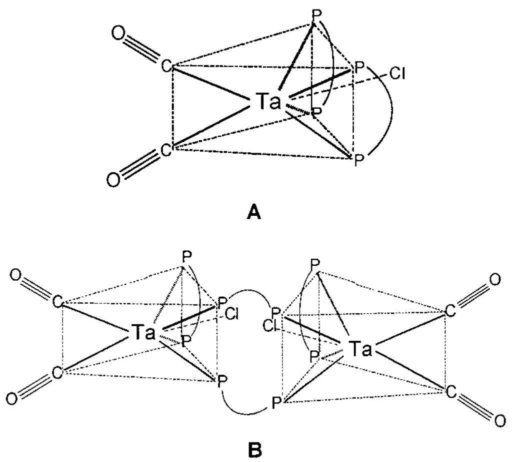

Figure 2. (A) Idealized structure of **1**. (B) Idealized structure proposed for **2**.

Synthesis and Characterization of [TaCl(CO)$_2$(dppe)$_2$]$_{2x}$ (2). During the synthesis of **1**, a second orange-colored compound **2** was also formed; the two compounds can be separated easily by column chromatography. Initially the presence of **2** in reaction mixtures was not noticed since the IR bands of the two compounds overlap considerably and the relative intensities of their bands are similar (see below). However, column chromatography on silica gel was found to be useful for the purification of **1**, and the product of the synthesis separated into two red bands which were distinguished on the basis of their IR and ^{1}H NMR spectra. Although **2** could not be characterized crystallographically, its formulation as an oligomer of **1** is reasonable on the basis of elemental analyses and the great similarity of the IR spectrum of **2** to that of **1**. Several attempts were made to obtain single crystals of **2** for crystallographic purposes, without success. Elemental analyses of **2** are consistent with the formulation, the proportion of carbon in the sample being marginally high because of the presence of traces of solvent (NMR) in the crystal lattice.

Also as was found for **1**, **2** is reasonably air-stable but is somewhat moisture-sensitive. The solid material may be handled in air for up to 1 h without any visible change, and the compound is very stable thermally. Attempts to convert **2** to **1** by heating solutions in toluene or acetonitrile at 50−60 °C overnight failed. Furthermore **2** does not react with carbon monoxide, as does **1**.

The IR (solution and solid) and Raman (solid) spectra of **2** exhibit two main carbonyl stretching bands at ~1820 and ~1720 cm^{-1}, and the spectra are thus consistent with mutually *cis* CO ligands, as observed for **1**. In addition, the similarities in the solution and the solid state spectra suggest that the same inner coordination sphere structure exists in the solid state and in solution. Interestingly, the carbonyl stretching bands of **1** and **2** in solution are very similar, both exhibiting a higher frequency, narrow, strong band and a lower frequency, broad, medium intensity band. In addition, the frequencies of the two bands of **1** differ by only ~14 and ~20 cm^{-1} from those of **2**, and it seems highly likely that these two compounds have essentially the same type of capped trigonal prismatic, 7-coordinate structure, with two carbonyl ligands located *cis* to one another.

The ^{1}H NMR spectrum of **2**, however, is very different from that of **1**. While the phenyl and methylene resonances of the latter are all broad, the resonances of **2** are sharp and well-resolved (Figure 3). While for **1**, the two *broadened* methylene resonances exhibit perhaps only slightly contact shifted reso-

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(11) Harris, R. K.; Olivieri, A. C. *Prog. NMR Spectrosc.* **1992**, *24*, 435.

(12) The methylene chemical shifts of free dppe, TaH(CO)$_4$(dppe), [Et$_4$N][Ta(CO)$_4$(dppe)], and W(CO)$_4$(dppe) all fall in the range δ 2.1−2.4.[1b]

(13) Lamar, G. N., Horrocks, W. D., Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(14) Felten, C.; Richter, J.; Priebsch, W.; Rehder, D. *Chem. Ber.* **1989**, *122*, 1617. The reported Nb−C bond lengths seem unusually long and may be in error.

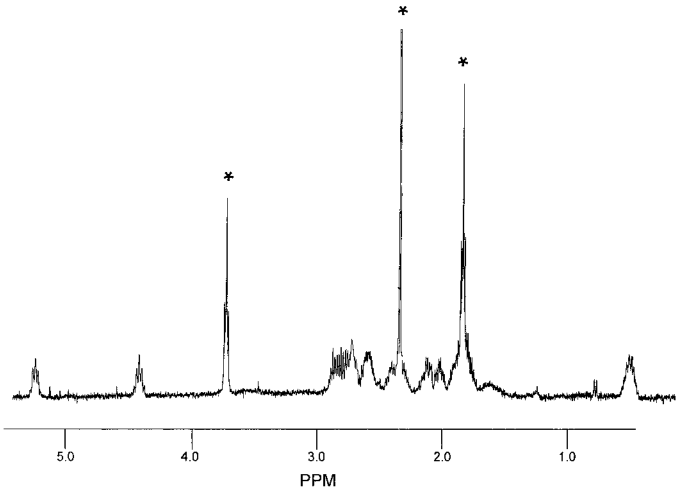

Figure 3. ^{1}H NMR spectrum of **2** in the region δ 0.2−5.4. Resonances marked with asterisks arise from traces of THF and toluene.

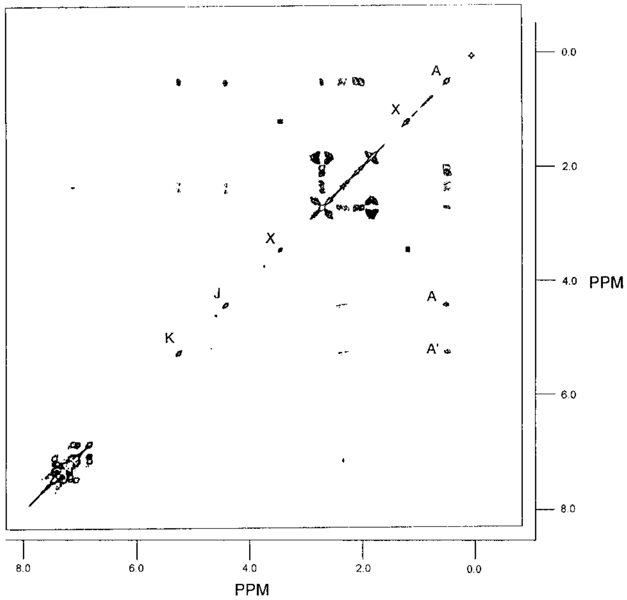

Figure 4. Full COSY spectrum of **2**.

nances (δ 2.52, 1.78 in toluene-d_8), the spectrum of **2** exhibits several *well-resolved* multiplets which are attributable to methylene hydrogens but which occur in the range δ 0.4−5.3 and possibly lower (see below). Thus, the resonances of **2** differ markedly from those of **1** in the way they are affected by the paramagnetism, on the one hand being much narrower, but on the other hand being very significantly contact shifted from the normal methylene region.

Careful analysis of the ^{1}H NMR spectrum of **2** suggests that there are at least eight separate methylene multiplets, the integrations of which are not all equivalent, and thus there are more than two dppe ligands present in this compound. Furthermore, by collecting NMR spectra over the temperature range from 298 to 193 K, it was possible to observe some of the multiplets separate further into two (or more) multiplets. Even at 193 K, the methylene resonances were found in the range δ 0.4−5.1, indicating that some paramagnetism is still present at this temperature.

In order to better interpret the ^{1}H NMR spectrum, a COSY experiment was carried out utilizing a solution of **2** in $CDCl_3$ at 298 K. The resulting COSY spectrum of the entire methylene region (δ 0.4−5.5) is shown in Figure 4, while an expansion of the region δ 0.4−3.2 is shown in Figure 5 (the resonances marked with an x are attributable to ethyl ether). To facilitate discussion, the relevant resonances are labeled A−K.

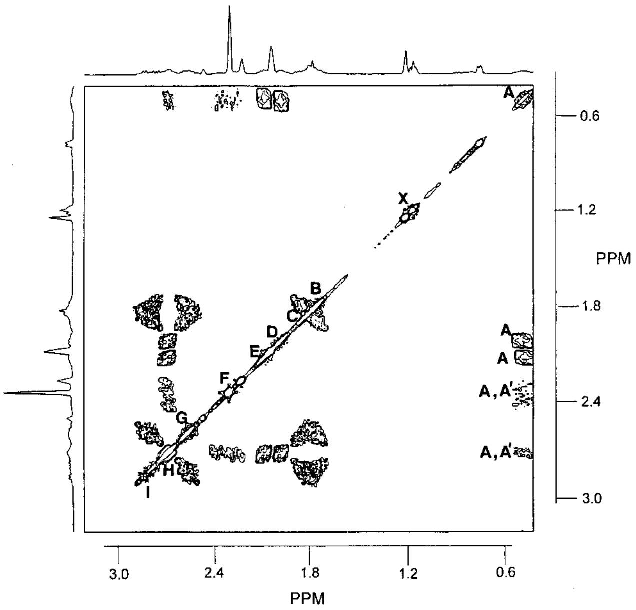

Figure 5. COSY spectrum of the methylene region (δ 0.4−5.5) of **2**.

Since there are two methylene groups per dppe ligand, it was anticipated that each hydrogen would be *J*-coupled to three others. However, inspection of Figure 4 indicates that the high-field resonance labeled A forms cross-peaks to at least five others, a conundrum which was at least partially solved when we realized that there are, in fact, two separate resonances at A, separated by less than 0.1 ppm (labeled A and A′ for clarity). Thus, there are cross-peaks between resonances A and A’ with lower field resonances at δ 5.3 (K) and at δ 4.4 (J), and more detailed analyses indicate further cross-peaks with the resonances labeled D−F and H. In the same way, a second group of resonances is formed by B, C, G, and I. In addition, two resonances labeled F can be identified, with couplings to A, A′, J, K, and H, and there is even an apparent cross-peak of F with a resonance at ∼δ 7.2.

Thus, the methylene resonances can be divided roughly into two groups, A, D−F, H, J, and K, integrating to nine hydrogens, and B, C, G, and I, apparently integrating to seven hydrogens. However, because of significant overlap, the integrations must be regarded only as approximate. In the final analysis, the COSY experiment implies that **2** contains sixteen separate hydrogens in two groups, and thus four dppe ligands, in pairs which are somehow different.

The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits four double doublet resonances of equal intensity, consistent with a structure containing pairs of dppe ligands in which all four phosphorus atoms are non-equivalent. To possibly aid in structural elucidation, a ^{31}P COSY experiment was performed at 298 K utilizing a solution of **2** in $CDCl_3$. It was apparent from the results that each phosphorus atom of **2** is coupled to all of the other three, but since each resonance in the one-dimensional spectrum is a double doublet, coupling of each nucleus to the “third” phosphorus is very weak. One-dimensional phosphorus spectra collected at temperatures to 193 K showed that the separation between these pairs of resonances decreased with temperature, possibly because of Curie law behavior.

As suggested above, the analytical data for **2** and the very close similarities in the IR and Raman spectra of **1** and **2** suggest that the inner coordination sphere of each tantalum atom of the latter assumes a capped trigonal pyramidal structure, as in **1**. Initially we considered a cyclic, dimeric structure with two bridging and two chelating dppe per dimer, as shown in idealized fashion in Figure 2B. This would contain two types of dppe ligands, bridging and chelating, and could be skewed such that all sixteen methylene hydrogens would be magnetically nonequivalent, as would all four phosphorus atoms. However, attempts to construct this structure using space-filling models failed for steric reasons; the CH_2CH_2 backbone of dppe is too short, and the projecting phenyl groups are too large. Higher repeating units, such as a cyclic tetramer, seem likely, but further speculation at this point is unwarranted. Mass spectra of the compound were uninformative, exhibiting primarily dppe, and since the compound invariably contains trace amounts of solvent, molecular weight determinations seemed pointless.

However, a basic repeating unit such as that shown in Figure 2B seems reasonable for three reasons. The inner coordination sphere is virtually identical to that of **1**, giving rise to the very similar electronic structures and which result in comparable IR and Raman spectra for **1** and **2**. On the other hand, one dppe each of **1** and **2** exhibit different denticities, giving rise to very different contact shifts and dissimilar chemistry. Possibly because of differences in strain, **1** reacts rapidly with CO under conditions where **2** is inert.

The solid state phosphorus NMR spectrum exhibits very broad resonances in the range δ 35−70, a similar chemical shift range to that of the solution spectra, but is not helpful in structural elucidation. The resonances are presumably broadened because of quadrupolar interactions with the tantalum.[11] The $^{13}C\{^1H\}$ NMR spectra of samples of **2** are also uninformative.

Interestingly, $^{31}P\{^1H\}$ NMR spectra of samples of **2** which had not been recrystallized exhibited weak (∼10% of the intensities of those of **2**) double doublet resonances of a second species; phosphorus resonances were observed at δ 59.3 (dd, J = 10.5, 83.8 Hz, 2P), 54.4 (d, J = ∼9, 83.3 Hz, 2P), 45.7 (d, 83.3 Hz, 2P), and 28.4 (dd, J = 12.0, 81.4 Hz, 2P). The ^1H NMR spectrum of **2** is sufficiently complicated that this second component could not be identified, and, after recrystallization, resonances of the second component were not observed in the $^{31}P\{^1H\}$ NMR spectrum.

Synthesis and Characterization of $TaCl(CO)_4(dppe)$ (3). Calderazzo *et al.*[3] have reported the preparations and IR spectra of the compounds $TaX(CO)_4(dppe)$ (X = Cl, Br, I); in all cases, syntheses were carried out in the absence of excess dppe because these compounds were found to be prone to substitution of CO to give $TaX(CO)_2(dppe)_2$. As previously reported,[1] reactions of the tantalum-centered radical $Ta(CO)_4(dppe)$ with organic halides RX (X = Cl, Br, I) result in the formation of the corresponding halo compounds $TaX(CO)_4(dppe)$, and thus we had reason to investigate the chloro compound $TaCl(CO)_4(dppe)$ **3** at least briefly. Furthermore, the ^1H NMR spectrum of **3** had not been reported, and we wished to assess **3** for paramagnetism.

Reaction of **1** with CO readily produces compound **3**, which was generated *in situ* to obtain spectral data because of the ready reversibility of the carbonylation reaction. IR data have been previously reported,[3] and the data we have obtained for **3** are in good agreement. The IR spectrum of a toluene solution exhibits ν_{CO} at 2025 (m), 1952 (w), 1904 (s), and 1885 cm^{-1} (m), consistent with a structure in which the four CO ligands are essentially mutually *cis*, as in the iodo analogue.[3] The ^1H NMR spectrum of **3** in toluene-d_8 exhibits, besides well-resolved phenyl resonances in the region δ 6.80−7.63, three somewhat broadened methylene multiplets at δ 2.90 (1H), 2.73 (1H), and 1.70 (2H). As with **2**, albeit to a lesser extent, the lower field, single hydrogen resonances appear to be somewhat contact shifted.

Magnetic Properties of 1−3. The Evans' method[5] was used to determine the magnetic susceptibilities of **1** and **2** over the temperature range 183−298 K, and of **3** at 298 K, in methylene chloride. The solutions contained 5.0% (v/v) each of cyclohexane and mesitylene for susceptibility shift ($\Delta\nu$) measurements. Concentrations were corrected for changes in the density of the solvent due to temperature, and $\Delta\nu$ for **1** was found to decrease from 9.7 Hz at 298 K to 6.7 Hz at 183 K, corresponding to gram susceptibilities[15] of 6.6×10^{-7} cm^3 g^{-1} and 6.2×10^{-7} cm^3 g^{-1}, respectively. In the case of **2**, the $\Delta\nu$ was found to decrease from 3.7 Hz at 298 K to 2.8 Hz at 223 K. Compound **3** was generated by the carbonylation of **1** ([**1**] = 0.0466 M) at 298 K and was investigated *in situ*. For this compound, $\Delta\nu$ = 6.2 Hz at 298 K, corresponding to a gram susceptibility of 6.8×10^{-7} cm^3 g^{-1}. While it is possible in principle to convert the gram susceptibilities to molar susceptibilities, make diamagnetic corrections[15] for the ligands, and then calculate magnetic moments for **1** and **3**, at least, the measured gram susceptibilities are very small and the diamagnetic corrections are comparable in magnitude because of the large molecular weights (∼1000 g mol^{-1}). In view of the uncertainties in the very approximate, available data for diamagnetic corrections, further speculation on the magnetic properties seems unwarranted.

Compounds **1**−**3** are all 18-electron compounds of Ta(I), and, thus, the observed degrees of observed paramagnetism, albeit slight, are surprising since organotransition metal compounds are normally low-spin and hence diamagnetic. However, there have been reported several examples of 18-electron, organometallic compounds of low symmetry and containing weak field ligands, which exhibit temperature-dependent equilibria between diamagnetic ground states and triplet excited states. Thus, the compounds η^5-$Cp'Mn(CO)_2L$ and η^6-$C_6H_6Cr(CO)_2L$ (Cp′ = substituted Cp; L = N-donor) exist to a significant extent in a high spin excited state at room temperature and exhibit temperature-dependent magnetic moments and well-resolved, unshifted ^1H NMR spectra, but not EPR spectra.[16a] More recently, the compound $[\eta^5\text{-}Cp^*Fe(CO)_2(acetone)][CF_3SO_3]$ has been reported to exhibit a magnetic moment of ∼2.9 μ_B, corresponding to two unpaired electrons, in the temperature range 77−300 K.[16b]

It is thus possible that the observed paramagnetism of **1**−**3** arises from proportions of the compounds existing in high-spin triplet states in which the magnetic moments are ∼2.83 μ_B.[15] Ignoring for the moment the caveat made above concerning converting the gram susceptibility of **1** to a net magnetic moment, the proportion of **1** present in the high-spin state at room temperature is ∼5%. Furthermore the frequency separation for **1** decreases as the temperature decreases, consistent with a diamagnetic ground state and with a decrease in the proportion of the compound which is in the high-energy state. In agreement with this hypothesis, the compound is diamagnetic in the solid state. Compound **1** is also EPR silent in liquid solution, presumably because of rapid exchange between the high- and low-spin states. The magnitudes of the susceptibility shifts of **2** and **3** are comparable to those of **1**, and presumably similar proportions of these compounds exist in the high-spin state although they have not been studied in as much detail.

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(15) (a) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968. (b) Abeles, T. P.; Bos, W. G. *J. Chem. Educ.* **1967**, *44*, 438. (c) Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: Toronto, 1976; Chapter 9.

(16) (a) Kaim, W.; Roth, T.; Olbrich-Deussner, B.; Gross-Lannert, R.; Jordanov, J.; Roth, E. K. H. *J. Am. Chem. Soc.* **1992**, *114*, 5693. (b) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1994**, 931.

However, **2** is also paramagnetic in solution and diamagnetic as a solid, and no EPR signal was observed, consistent with this proposal.

The methylene resonances of **1**−**3** in the ^{1}H NMR spectra exhibit notable contact shifts,[13] especially those of **2**, for which significant shifts to lower field of ∼0.16 ppm on going from 298 to 193 K (in contrast to the much smaller shifts of diamagnetic markers) are noted. While temperature dependence of chemical shifts is anticipated,[13] the spectral parameters are weighted averages of the parameters of all species in equilibrium in solution and thus the contact shifts cannot be analyzed. It is not clear why the $^{31}P\{^1H\}$ chemical shifts seem so little affected; significant variations with temperature are observed, but one might expect significant broadening from spin density being delocalized onto the ligand donor atoms.[13]

There are two other possible rationales for the paramagnetism observed for **1**−**3**. It is conceivable, for instance, that the sterically very crowded compounds dissociate to some extent to give paramagnetic, six-coordinated 16-electron compounds containing dangling dppe ligands.[17] The diamagnetism observed for the solid materials would be consistent with this hypothesis, and **1** and **3**, at least, are very substitution labile, possibly via a dissociative mechanism. While it seems unlikely that **1**−**3** would all dissociate to the same extent, the question remains moot.

It is also possible that all three compounds exhibit temperature-independent paramagnetism arising from mixing of the ground states with thermally unpopulated, yet low-lying, paramagnetic excited states.[15] Such cases are well-represented in the literature and give rise, even in low-spin, 18-electron octahedral cobalt(III) complexes, to temperature-independent paramagnetism of magnitudes similar to those observed here.[15] Arguing against this hypothesis is our observation of temperature-*dependent* paramagnetism and apparent diamagnetism in the solid state.

The degree to which our findings may be extended to similar seven-coordinated compounds of tantalum(I) is not clear, although we note that the methylene resonances of many other compounds of the type $TaX(CO)_2L_4$ are described as being broad and unresolved.[4b] This is in itself perhaps a hint of similar interesting properties of these compounds, since $TaH(CO)_4$(dppe) and $[Et_4N][Ta(CO)_4(dppe)]$, for instance, exhibit quite sharp resonances for the methylene hydrogens of the coordinated dppe.[1b]

Summary

$TaCl(CO)_4$(dppe) reacts reversibly with dppe to form $TaCl(CO)_2(dppe)_2$, which assumes a capped trigonal prismatic structure in the solid state and in solution. These two 18-electron compounds exhibit paramagnetism in solution, consistent with small proportions of both existing in a high-spin (triplet) state and rationalizing broadening and/or shifting of resonances in the ^{1}H NMR spectra. During the synthesis of $TaCl(CO)_2(dppe)_2$ (**1**), there is formed a second compound which exhibits carbonyl stretching bands very similar to those of $TaCl(CO)_2(dppe)_2$. The new species is formulated as $[TaCl(CO)_2(dppe)_2]_{2x}$ ($2x \geq 4$), based on a wide variety of spectroscopic data, and also exhibits paramagnetism. In this case, resonances in the ^{1}H NMR spectrum are sharp, but the methylene resonances exhibit large contact shifts.

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Supporting Information Available: ORTEP diagram of **1** showing 30% probability displacement ellipsoids and the numbering scheme for all non-hydrogen atoms. Tables of crystallographic data for **1**, bond lengths and angles, anisotropic displacement parameters, hydrogen atom fractional coordinates and isotropic displacement parameters, and fractional coordinates of toluene solvate molecules (14 pages). Ordering information is given on any current masthead page.

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[17] For recent examples of such behavior, see: (a) Abugideiri, F.; Keogh, D. W.; Poli, R. *J. Chem. Soc., Chem. Commun.* **1994**, 2317. (b) Jolly, P. W.; Kopiske, C.; Krüger, C.; Limberg, A. *Organometallics* **1995**, *14*, 1885. (c) Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *147*, 11745.