Synthesis and Properties of $Ta(CO)_4(dppe)$, the First Stable Mononuclear Tantalum(0) Carbonyl Compound

MaryAnn D. Koeslag and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

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Summary: Reaction of the hydride $TaH(CO)_4(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane) in benzene with the tris(p-tert-butylphenyl)methyl radical results in abstraction of the metal-bonded hydrogen atom and formation of tris(p-tert-butylphenyl)methane and the 17-electron compound $Ta(CO)_4(dppe)$. The latter is the first tantalum(0) carbonyl compound to be synthesized and studied.

Although $V(CO)_6$ and several of its derivatives have been known for many years,[1] the chemistry of zerovalent, binary metal carbonyl compounds of the heavier group 5 metals niobium and tantalum has been much slower to develop. While a small number of zerovalent compounds of niobium and tantalum (including $Ta(CO)_6$ at 35 K) have been synthesized by metal vaporization techniques,[2] attempts to synthesize $M(CO)_6$ (M = Nb, Ta) or their derivatives in solution by either reductive carbonylation of metal salts or oxidation of carbonylate complexes $[M(CO)_{6-n}L_n]^-$ (M = Nb, Ta) have invariably resulted in the formation of complexes of the metals in oxidation states other than zero.[1a,b,3]

We[4] and others[5] have recently demonstrated the utilization of persistent triarylmethyl radicals $Ar_3C^\bullet$ to abstract hydrogen atoms from 18-electron transition-metal hydride complexes MHL_n and form the corresponding 17-electron compounds ML_n (eq 1). In the absence of suitable

$$MHL_n + Ar_3C^\bullet \rightarrow ML_n + Ar_3CH \qquad (1)$$

radical traps, the species ML_n may couple and the organometallic products obtained are often the 18-electron, diamagnetic dimers $[ML_n]_2$. However, the possibility of synthesizing zerovalent compounds of niobium and tantalum by abstracting hydrogen atoms from hydrides of the types $MH(CO)_{6-n}L_n$ (M = Nb, Ta; L = tertiary phosphines)[3c,6] is apparent, and we describe herein the results of our initial attempts to synthesize novel zerovalent compounds of the type $Ta(CO)_4L_2$.

The compound $TaH(CO)_4(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane)[3c,6c] was reacted in benzene with slightly greater than 1 molar equiv of a solution of the tris(*p*-*tert*-butylphenyl)methyl radical[5c] in the dark and at 285 K or lower (eq 2). The orange hydride solution

$$TaH(CO)_4(dppe) + (t\text{-}BuC_6H_4)_3C^\bullet \rightarrow Ta(CO)_4(dppe) + (t\text{-}BuC_6H_4)CH \qquad (2)$$

immediately darkened and turned brown; the solvent was removed after 15 min, yielding a brown powder, which was washed repeatedly with hexanes. The product, $Ta(CO)_4(dppe)$, is always obtained contaminated with dppe and a small quantity of organic species. It is also very labile thermally and cannot be obtained analytically pure or as single crystals suitable for X-ray diffraction studies.[7] Identification has therefore been made on the basis of its magnetic and spectroscopic properties.

Measurement of the magnetic moment of $Ta(CO)_4(dppe)$ was carried out utilizing the Evans method[8] on benzene-d_6 and toluene-d_8 solutions containing reaction mixtures resulting from treatment of $TaH(CO)_4(dppe)$ with slight deficiencies of $(t\text{-}BuC_6H_4)_3C^\bullet$. Careful integration of the NMR spectra permitted accurate determination of the concentrations of $TaH(CO)_4(dppe)$ and $(t\text{-}BuC_6H_4)_3CH$ and, by difference, of $Ta(CO)_4(dppe)$.[9] The magnetic moment of a 1.40×10^{-2} M solution of $Ta(CO)_4(dppe)$ at 298 K, corrected for diamagnetic contributions,[10] was $1.7 \pm 0.1\ \mu_B$, very close to the spin-only value (one unpaired electron) expected for a low-spin, d^5 octahedral complex.[10] Interestingly, however, the magnetic moment was found to be strongly temperature dependent, decreasing smoothly and reversibly to $1.4 \pm 0.1\ \mu_B$ at 213 K, and thus $Ta(CO)_4(dppe)$ appears to dimerize partially in solution to the 18-electron, metal–metal-bonded $[Ta(CO)_4(dppe)]_2$. Assuming an equilibrium between a doublet state monomer and a diamagnetic dimer (the compound is diamagnetic in the solid state[11]), as in eq 3, calculations

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[7] The compound is very air and heat sensitive and deteriorates slowly under nitrogen as a solid even at 243 K. Solutions decompose significantly under argon within 1 h above 285 K in benzene or toluene and within seconds in polar solvents.

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[9] Since workup of solutions of $Ta(CO)_4(dppe)$ always results in partial decomposition and the release of some free dppe, the indirect approach described seemed superior to attempting to prepare solutions of known concentrations of $Ta(CO)_4(dppe)$ by weighing "purified" material. That no tris(*p*-*tert*-butylphenyl)methyl radical was present was shown by the absence of its resonance in the EPR spectrum. See: Dünnebacke, D.; Neumann, W. P.; Penenory, A.; Stewen, U. *Chem. Ber.* **1989**, *122*, 533.

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Table 1. IR and Raman Data for the Compounds $M(CO)_4(dppe)$ and $Et_4N[M(CO)_4(dppe)]$ (M = V, Ta)

compd	ν_{CO} (cm^{-1})	comments
$Ta(CO)_4(dppe)$	1963 (m), 1893 (m), 1880 (vs, br)[a]	IR in toluene
$V(CO)_4(dppe)$	1985 (s), 1889 (s), 1870 (vs), 1849 (vs)[19a]	IR in Nujol
$Et_4N[Ta(CO)_4$-(dppe)]	1906 (m), 1799 (vs), 1779 (m), 1750 (m)[a]	IR in THF
$Et_4N[V(CO)_4$-(dppe)]	1903 (s), 1799 (vs), 1780 (vs), 1747 (m)[19b]	IR in THF
$[Ta(CO)_4(dppe)]_2$	1958 (m), 1870 (vs, br), 1830 (s), 1793 (s)[a]	IR in Nujol
$[Ta(CO)_4(dppe)]_2$	1960 (m), 1881 (s), 1823 (m), 1812 (m, sh), 1799 (sh)[a]	Raman in Nujol

[a] This work.

$$[Ta(CO)_4(dppe)]_2 \rightleftarrows 2Ta(CO)_4(dppe) \qquad (3)$$

based on the variable-temperature magnetic susceptibility data suggest that K_{eq} varies between 2.8×10^{-2} mol L^{-1} at 213 K and 1.4×10^{-1} mol L^{-1} at 283 K. It was also determined that $\Delta H = 2.7 \pm 0.4$ kcal mol^{-1} and $\Delta S = 5.5 \pm 0.2$ cal mol^{-1} K^{-1}; at 213 K, ~60% of the tantalum is present as monomer. The tantalum(0) system thus stands in strong contrast to many vanadium(0) analogues, for which metal–metal bond formation has not been observed,[1c,d] and we note that metal–metal bonds involving the heavier transition metals are normally stronger than those in the corresponding compounds of the 3d metals.[12] On the other hand, the enthalpy change for eq 3 is considerably less than those for dissociation to metal-centered radicals of $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$,[13a] $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$,[13b] or $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$,[13b] possibly implying that any metal–metal bond in $[Ta(CO)_4(dppe)]_2$ may be very weak.

Formation of the dimer is supported by observations of major differences between the solution IR and the solid-state IR and Raman spectra of $Ta(CO)_4(dppe)$. IR and Raman[14] data for the compound in the carbonyl stretching region are listed in Table 1, where analogous data for the compounds $V(CO)_4(dppe)$ and $Et_4N[M(CO)_4(dppe)]$ (M = V, Ta) are also listed for purposes of comparison. The monomeric complexes presumably assume essentially *cis*-octahedral structures, and all should exhibit four carbonyl stretching normal modes in both the IR and the Raman spectra.[15a] As can be seen, the IR solution spectrum of $Ta(CO)_4(dppe)$ and the IR/Raman spectra of the three other complexes of this stoichiometry all exhibit the expected four bands,[15b] the average of the frequencies of the two neutral species differing by only 12 cm^{-1} but being some 70–90 cm^{-1} higher than the averages of the frequencies of the anionic species, as anticipated. It is clear from Table 1 that the IR and Raman spectra of solid $Ta(CO)_4$(dppe) are very different from the solution IR spectrum, and thus this compound exists in different forms in solution and in the solid state, consistent with the monomer–dimer equilibrium of eq 3. Moreover, observation of bands in the region 1790–1830 cm^{-1} in the spectra of the solid suggests that the dimer may contain bridging carbonyl groups.

Ambient-temperature ^1H NMR spectra of $Ta(CO)_4$(dppe) in benzene-d_6 or toluene-d_8 are notable for the absence of obvious resonances. Only after many accumulations were very broad proton resonances readily observed in the ranges δ 6.5–8.0 and 0–3.5, no other resonances being detected in the range ±1150 ppm. It thus appears that the ^1H nuclei of the radical experience very rapid relaxation, as anticipated, but only small isotropic shifts.[16]

The ^{31}P NMR spectrum in toluene-d_8 is also devoid of resonances at room temperature, but broad resonances at δ 81, 71, 61, 50, and 36 were observed at 190 K, very similar to the chemical shifts of broad resonances observed in MAS ^{31}P spectra (δ 85, 60, 34) of the compound in the solid state.[17] Apparently because of the facile monomer–dimer exchange, all attempts to obtain EPR spectra were unsuccessful; no resonances could be observed for either liquid benzene solutions at ambient temperature or frozen benzene solutions down to 11 K.

Characteristic of 17-electron compounds,[1d] $Ta(CO)_4$(dppe) reacts rapidly in high yields (judging from relative IR intensities) in toluene with halogen donors such as benzyl bromide, allyl bromide, and *tert*-butyl iodide, forming as primary products the compounds $TaX(CO)_4$(dppe) (X = Br, I) (X = Br, ν_{CO} 2024, 1952, 1903, and 1885 cm^{-1}; X = I, ν_{CO} 2023, 1948, 1904, and 1880 cm^{-1}).[3c] When these reactions were carried out in the absence of CO (under argon), or when the solvent was subsequently removed under reduced pressure, the complexes $TaX(CO)_2(dppe)_2$ were formed subsequently (ν_{CO} in toluene 1837, 1765 cm^{-1}).[18] The hydride, $TaH(CO)_4(dppe)$, and the anionic complex, $Et_4N[Ta(CO)_4(dppe)]$, react very slowly, if at all, with the same alkyl halides in toluene.

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(11) Magnetic susceptibilities of solid samples were measured on a Johnson Matthey magnetic susceptibility balance.

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(14) An FT-Raman spectrum of $Ta(CO)_4(dppe)$ as a powder could not be obtained, since the sample was decomposed by the YAG laser even at the lowest power setting. Success was instead achieved using a suspension of the solid in Nujol, which acts as a heat sink.

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

(17) Splitting of solid-state resonances may also arise from interactions with ^{181}Ta ($I = 7/2$). See: Harris, R. K.; Olivieri, A. C. *Prog. NMR Spectrosc.* 1992, *24*, 435.

(18) For the corresponding dmpe complexes, see: Datta, S.; Wreford, S. S. *Inorg. Chem.* 1977, *16*, 1134. For the generation of $TaX(CO)_2(dppe)_2$, the second dppe arises from prior, partial decomposition of $Ta(CO)_4$(dppe).

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