

Synthesis and Properties of the 17-Electron, Tantalum-Centered Radical $\text{Ta}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$

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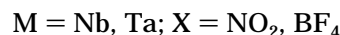
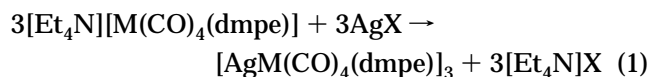
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The novel 17-electron compound $\text{Ta}(\text{CO})_4\text{dppe}$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is formed via hydride hydrogen atom abstraction from $\text{TaH}(\text{CO})_4\text{dppe}$ by the tris(*p*-*tert*-butylphenyl)methyl radical. The compound exists in solution as an equilibrium mixture of monomer (the dominant species) and carbonyl-bridged dimer $[\text{Ta}(\text{CO})_4\text{dppe}]_2$ but solely as the latter in the solid state. It is very labile but was characterized electrochemically, IR, Raman, and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopically, and chemically. Typical of metal-centered radicals, $\text{Ta}(\text{CO})_4\text{dppe}$ abstracts halogen atoms from organic halides RX to give the halotantalum compounds $\text{TaX}(\text{CO})_4\text{dppe}$ and, in some cases, $\text{TaR}(\text{CO})_4\text{dppe}$. Cyclic voltammetry experiments show that the oxidation of $[\text{Ta}(\text{CO})_4(\text{dppe})]^-$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ is a one-electron process, irreversible at scan rates below 50 V/s. The formal potential of $[\text{Ta}(\text{CO})_4(\text{dppe})]^{0/-}$ is estimated as -1.2 V vs ferrocene. The reduced lifetime of the radical is ascribed to reactions with the ionic medium, the main electrochemical oxidation products being $\text{TaH}(\text{CO})_4(\text{dppe})$ and $\text{TaCl}(\text{CO})_2(\text{dppe})_2$.

Although 17-electron, metal-centered radicals have been characterized for many transition metals,¹ such complexes of the group 5 metals, vanadium, niobium, and tantalum, have been isolated only in the case of vanadium. Indeed, $\text{V}(\text{CO})_6$ was reported over 30 years ago² and remains unique among this class of compounds because it is a stable radical and its derivatives were characterized long before metal-centered radicals were recognized as possibly being common and of general interest. Furthermore, even now, $\text{V}(\text{CO})_6$ is the only simple binary metal carbonyl complex to be isolated as a radical monomer which is thermally stable to dimerization,² and its electronic structure has been the subject of intense study.^{2–5} $\text{V}(\text{CO})_6$ readily undergoes carbonyl substitution with neutral, soft ligands (L) such as phosphines, forming 17-electron monomers of the general formula $\text{V}(\text{CO})_{4-n}\text{L}_n$ ($n = 1–4$).⁶ In general, the substituted carbonyl complexes are more thermally stable than is $\text{V}(\text{CO})_6$, and many have been isolated at room temperature. In contrast, treatment of $\text{V}(\text{CO})_6$ with hard Lewis bases B results in disproportionation to vanadium(II) and $-(\text{I})$ species $[\text{VB}_6]^{2+}$ and $[\text{V}(\text{CO})_6]^-$.^{6b}

Although vanadium(0) complexes are thus well-documented, the corresponding monomeric complexes of niobium(0) and tantalum(0) have not been isolated. The neutral hexacarbonyl of tantalum has been tentatively identified in argon matrices by comparison with the infrared spectrum of $\text{V}(\text{CO})_6$,^{7a} but neither $\text{Nb}(\text{CO})_6$ nor $\text{Ta}(\text{CO})_6$ has been observed under ambient conditions. In 1989, Calderazzo *et al.*^{8a} reported the synthesis of cluster complexes, $[\text{AgM}(\text{CO})_4\text{dmpe}]_3$ ($\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane), in which niobium and tantalum were proposed to be present in the zero oxidation state (eq 1). These complexes were character-



ized by single-crystal X-ray diffraction,⁸ which showed that the structures consist of heterometallic rafts in which the metal atoms are arranged in almost equilateral triangles with tantalum atoms at the vertices of a large triangle and silver atoms at the midpoints of each side. On the basis of the short Ag–Ag bonds (2.842

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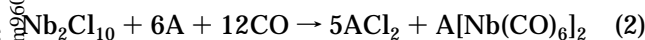
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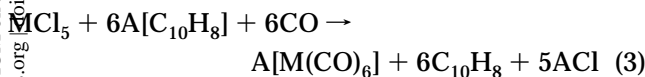
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Å for the Nb and Ta complexes, compared to 2.883 Å in silver metal) and the Ag–M bond lengths (2.888 Å) which compare favorably to the sums of the metallic radii (2.91 Å), these clusters were characterized as complexes of niobium(0) and tantalum(0), although no evidence for dissociation to odd-electron Nb(0) or Ta(0) species has been noted.

Attempts to synthesize simple complexes of niobium(0) or tantalum(0) have begun with diamagnetic, 18-electron complexes in the -1 (d^6) and $+1$ (d^4) oxidation states. By effecting one-electron oxidations or reductions, respectively, of these types of complexes, one may in principle obtain the desired 17-electron radicals, and many such attempts have been made. The 18-electron, octahedral carbonylate ions $[M(\text{CO})_6]^-$ ($M = \text{V}, \text{Nb}, \text{Ta}$) have been prepared via reductive carbonylation of the chloro compounds VCl_3 ,^{9a} $\text{Nb}_2\text{Cl}_{10}$,^{9b} and TaCl_5 ,^{9b} respectively, in high yield, atmospheric pressure syntheses of $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$ being first reported some years ago.¹⁰ Thus Calderazzo *et al.*^{10a} described the synthesis of $[\text{Nb}(\text{CO})_6]^-$ using magnesium and zinc as reducing agents (eq 2), while Ellis *et al.*^{10b,e} reported the synthesis of both hexacarbonylates using alkali metal naphthalenides (eq 3).



A = Mg/Zn; yield = 39%

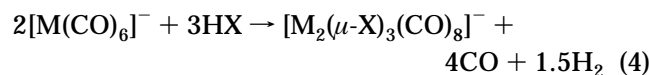


M = Nb, Ta; A = Na, Li; yields = 30–50%

As salts of bulky cations, the hexacarbonylates are thermally and chemically quite stable.^{10b–d} The solid materials $\text{Z}[\text{Ta}(\text{CO})_6]$ ($\text{Z} = n\text{-Bu}_4\text{N}^+$, Et_4N^+ , or PPh_4^+) can be handled in air for short periods of time, but solutions of all such complexes are very air sensitive.^{10b} The salts $\text{Z}[\text{V}(\text{CO})_6]$ are reported to be inert to thermal CO substitution,^{10d} but synthesis of substituted carbonylates can be achieved under photolytic conditions, generating $[\text{M}(\text{CO})_{6-n}\text{L}_n]^-$ ($n = 1–3$). Phosphine- and arsine-substituted carbonylates were reported to be rather reactive under various conditions,^{10c} but substituted complexes formed with chelating ligands are generally substantially more stable thermally and less air-sensitive than complexes containing two monodentate phosphines.^{10c}

The possibility of effecting a one-electron oxidation of the hexacarbonylate anions of niobium and tantalum to form the neutral hexacarbonyls has proven to be a tantalizing but, as yet, unattainable goal. Instead, two-electron oxidations have always been observed to occur although a variety of oxidizing agents has been used. For instance, when $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$ were

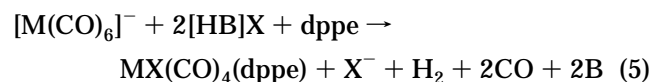
reacted with protonic acids, anionic dimeric complexes were obtained (eq 4).^{11a–c}



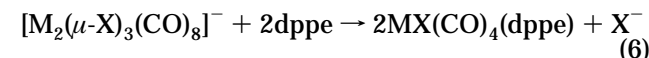
M = Nb, Ta; X = Cl, Br, I, MeCO_2

The same complexes have also been isolated from the reactions of $[\text{Nb}(\text{CO})_6]^-$ with a variety of metal halides and protonated bases.^{11b–d}

In view of the greater stability of substituted vanadium(0) carbonyl complexes, attempts have also been made to generate $\text{M}(\text{CO})_{6-n}\text{L}_n$ ($M = \text{Nb}, \text{Ta}$; L = tertiary phosphines) by either reaction of the hexacarbonylate anions in the presence of stabilizing ligands or by reaction of the corresponding substituted anionic complex. The reaction of $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$ with protonated bases was carried out with dppe added to the reaction mixture (eq 5).^{11c} The product of the

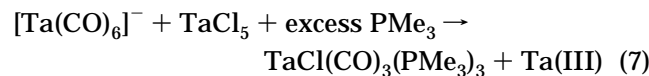


reaction was not the 17-electron radical, $\text{M}(\text{CO})_4(\text{dppe})$, but rather a substituted halo complex. Again two-electron oxidation processes had occurred, although the product was monomeric in the presence of the phosphine. By reaction of the anionic dimer with dppe, the same monomeric halo complex was obtained (eq 6).^{11c}



X = Cl, I

A similar reaction was also attempted with $[\text{Ta}(\text{CO})_6]^-$ and TaCl_5 , in the presence of PMe_3 (eq 7).¹² In this case



the product was the substituted tricarbonyl halo-complex, which was obtained in ~75% yield (based on the hexacarbonylate) although no tantalum-containing byproduct was identified.¹² The authors argued that, since $[\text{Ta}(\text{CO})_6]^-$ does not react with PMe_3 at room temperature, PMe_3 substitution in these reactions must occur via a 17-electron radical, $\text{Ta}(\text{CO})_6$, or a halogeno species, $\{\text{Ta}(\text{CO})_6\text{X}\}$. Since the reaction occurred under mild reaction conditions, substitution via a 17-electron radical was postulated to be more likely.¹²

Reactions of niobium(I) and tantalum(I) complexes with reducing agents have been no more successful at producing zerovalent complexes than have the attempted oxidations of the anionic complexes; two-electron reductions have always been observed. Thus several attempts have been made to reduce complexes of the general formulas $\text{MX}(\text{CO})_4\text{L}_2$ and $\text{MX}(\text{CO})_2\text{L}_4$ (M

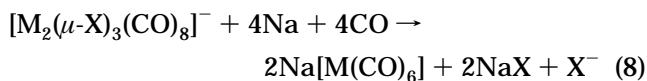
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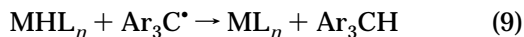
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= Nb, Ta; X = Cl, Br, I) but to no avail.^{8c,13} For instance, Lippard *et al.* attempted the reaction of equimolar quantities of TaCl(CO)₂(dmpe)₂ and sodium naphthalenide, but a mixture of the starting material and [Ta(CO)₂(dmpe)₂]⁻, resulting from a two-electron reduction, was obtained.^{13a} In those cases where two or more equivalents of a reducing agent (sodium or sodium naphthalenide) were used, [Ta(CO)₂(dmpe)₂]⁻ was the only product.¹³ Reduction of the anionic complexes discussed above also results in formation of the hexacarbonylates (eq 8).^{11b}



From the above discussion, it is apparent that a great number of oxidation and reduction reactions have been attempted for the synthesis of 17-electron radicals of niobium(0) and tantalum(0) without any success. The +1 and -1 oxidation states are apparently too readily accessible to allow one-electron processes to occur, and therefore a different approach must be utilized if complexes of Nb(0) or Ta(0) are to be synthesized.

As part of the development of new methodologies for the synthesis of novel 17-electron species, we^{14ab} and others¹⁵ have demonstrated the utility of persistent triarylmethyl radicals Ar₃C[•] to abstract hydrogen atoms from 18-electron, transition metal hydride complexes of the type MHL_n and form the corresponding 17-electron compounds ML_n (eq 9). In the absence of suitable radical



if any, the species ML_n may couple and the organometallic products obtained are often the 18-electron, diamagnetic dimers [ML_n]₂. On the other hand, in those cases where radical coupling is not feasible for steric reasons, the chemistry of eq 9 provides a very convenient route to new 17-electron compounds. Since a number of sterically hindered metal hydrides of the types MH(CO)₄L₂ and MH(CO)₂L₄ (M = Nb, Ta) are available, it seemed possible that the corresponding metal-centered radicals M(CO)₄L₂ and M(CO)₂L₄ (or their dimers) might also be synthesized via abstraction of the hydridic hydrogen atoms with triarylmethyl radicals.

While we have previously utilized the triphenylmethyl (trityl) radical,^{14a,b} the tris(*p*-*tert*-butylphenyl)methyl radical has been used in studies of the kinetics of hydrogen abstraction from organometallic hydride complexes,^{15c} and the tris(*p*-*tert*-butylphenyl)methyl group has the advantage that the ¹H NMR spectra of derivatives exhibit sharp, readily identified and integrated methyl resonances. Furthermore, Norton *et al.*^{15c} have published several methods for the generation of

this radical from the bromo precursor, with yields of the radical approaching 100%, and therefore we decided to work with the the tris(*p*-*tert*-butylphenyl)methyl radical.

The tantalum complex TaH(CO)₄(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) was chosen as a suitable starting material for our initial study of hydrogen abstraction reactions with tris(*p*-*tert*-butylphenyl)methyl because it has been reported to be stable under nitrogen at low temperatures for some weeks. A preliminary account of this work has appeared,^{14c} and we now describe this investigation in detail, providing as well improved synthetic procedures for the precursors Et₄N[Ta(CO)₄(dppe)] and TaH(CO)₄(dppe). We also report details of an investigation of the electro-oxidation of the former.

Experimental Section

Unless otherwise stated, all experiments were performed under argon (passed through a heated column of BASF catalyst to remove traces of oxygen and through a column of molecular sieves to remove traces of water) using standard Schlenk line techniques or in a Vacuum Atmospheres glove box under a nitrogen atmosphere. All solvents were dried under nitrogen: ethyl ether, toluene, benzene, and pentane over sodium; hexanes, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) over potassium; acetonitrile and dichloromethane over calcium hydride. Benzene used for reactions of (*t*-BuC₆H₄)₃C[•] was freeze-thaw degassed at least three times prior to use, as were all deuterated solvents for NMR. Other solvents were deoxygenated by bubbling with argon for a period of at least 30 min. Carbon monoxide was used as received; the cylinders were not emptied below 500 psig since water was found to contaminate the last portion of the cylinder gas. Chemicals were purchased from Aldrich, Strem, and BDH and were used as received.

IR spectra were collected on Bruker IFS-85 or IFS-25 FT-IR spectrometers, on samples in solution or as Nujol mulls. Raman spectra were obtained using a Bruker RFS-100 FT-Raman spectrometer, in most cases on finely-powdered solid samples which had been placed in 5 mm glass tubes. For Ta(CO)₄(dppe), a spectrum could not be obtained in this way because the solid was overheated by the YAG laser at all power settings; solid samples were therefore mixed with Nujol, which acted as a heat sink and thus allowed collection of spectra without thermal degradation of the samples. IR and Raman spectral data are given in Tables 1-4. UV-vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer.

Solution NMR spectra were recorded on Bruker AM-400 and ACF-200 FT spectrometers; the chemical shift references used for solution spectra were TMS for ¹H NMR and external H₃PO₄ for ³¹P{¹H} NMR. For ¹H NMR, 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 samples tightly packed into a MAS sample tube. For ¹³C, the reference used was adamantane (external); for ³¹P, spectra were referenced to dppe (internal, δ = -12.0). EPR spectra were recorded at the National Research Council, Ottawa, by Drs. K. Preston and P. Kaiser on a Varian E12 spectrometer equipped with a Bruker ER035M gaussmeter and a Systron-Donner microwave frequency counter. The magnetic susceptibilities of solid samples were measured on a Johnson Matthey magnetic susceptibility balance, and those of samples in solution, using the Evans NMR method.^{16a-c}

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Electrochemical measurements were carried out in a drybox under N₂. Reagent grade solvents were distilled from drying agents (CaH₂ for CH₂Cl₂, K for THF) under vacuum. The supporting electrolyte [Bu₄N][PF₆] was vacuum dried at 373 K after recrystallization from ethanol. Platinum electrodes were pretreated by polishing with diamond paste. Platinum disks constructed from wire of diameter 125 or 495 mm (Goodfellow, Inc.) were used in rapid scan experiments to minimize ohmic loss. Virtually identical responses were also obtained at gold and glassy carbon electrodes. PARC 173 or 273 potentiostats were used for all electrochemical measurements.

Potentials in this paper are referred to the ferrocene/ferrocenium couple, although the experimental reference electrode was a silver wire anodized in HCl media to produce a Ag/AgCl electrode. Our quoted potentials may be converted to the aqueous SCE potential scale by addition of +0.46 V for CH₂Cl₂ or +0.56 V for THF. Solutions of [Et₄N][Ta(CO)₄(dppe)] were always kept at 273 K or lower in order to minimize decomposition.

Tris(*p*-*tert*-butylphenyl)methyl Bromide, (*t*-BuC₆H₄)₃CBr. This was synthesized by the method of Colle and Lewis for the chloro analogue.¹⁷ Recrystallization from toluene yielded (*t*-BuC₆H₄)₃CBr as a white powder (11.2 g, 33%). ¹H NMR in C₆D₆: δ 7.48 (d, *J* = 8.6 Hz, 6H, phenyl H), 7.09 (d, *J* = 8.6 Hz, 6H, phenyl H), 1.17 (s, 27H, Me). ¹H NMR in CDCl₃: δ 7.16 (d, *J* = 8.7 Hz, 6H, phenyl H), 7.07 (d, *J* = 8.6 Hz, 6H, phenyl H), 1.20 (s, 27H, Me).

Tris(*p*-*tert*-butylphenyl)methyl, (*t*-BuC₆H₄)₃C[•].^{15c} (*t*-BuC₆H₄)₃CBr (100 mg, 0.203 mmol) and Zn powder (500 mg, excess) were weighed into a flask, which was wrapped in aluminum foil because of the light sensitivity of the radical. Indeed, all reaction vessels, syringes, and cuvettes were wrapped in foil. Benzene (25.0 mL) was added and the reaction was stirred at room temperature for 3 h. After the solids were allowed to settle (10–15 min), the required volume of radical solution was removed by syringe or cannula. Initially, the yield of the radical was determined by UV–vis spectroscopy (for the radical, λ_{max} = 524 nm and ε = 825 M⁻¹ cm⁻¹).^{15c} By using this method, the yield of (*t*-BuC₆H₄)₃C[•] was consistently ca. 80%. This reaction could be scaled up to 500 mg of (*t*-BuC₆H₄)₃CBr, the yield remaining approximately the same.

Tris(*p*-*tert*-butylphenyl)methane, (*t*-BuC₆H₄)₃CH. A suspension of (*t*-BuC₆H₄)₃CBr (300 mg, 0.610 mmol) in ethyl ether was treated with excess LiAlH₄. The original white suspension turned yellow immediately, but the color slowly disappeared and the solid dissolved. The reaction was stirred at room temperature for 30 min, quenched with ethanol, and filtered. Water was added to precipitate the product from the solution. The pale yellow solid was air-dried. Yield: 250 mg (99%). ¹H NMR in C₆D₆: δ 7.19 (m, 12H, phenyl H), 5.54 (s, 1H, CH), 1.21 (s, 27H, Me). Lit. (CDCl₃):¹⁷ δ 7.11 (m, 12H, phenyl H), 5.38 (s, 1H, CH), 1.27 (s, 27H, Me).

W(CO)₄(dppe). W(CO)₄(dppe) was synthesized using the method of Chatt *et al.*¹⁸ Recrystallization from toluene yielded W(CO)₄(dppe) as a pale yellow solid (3.2 g, 52%). IR (toluene): ν_{CO} 2017 (m), 1917 (s), 1904 (vs), 1887 cm⁻¹ (s). Lit.¹⁸ (CHCl₃): ν_{CO} 2020 (m), 1920 (sh), 1903 (s), 1885 cm⁻¹ (sh). Raman (powder): ν_{CO} 2013 (s), 1901 (vs), 1854 (vs), 1810 cm⁻¹ (vw). ¹H NMR in toluene-*d*₆: δ 7.50 (m, 8H, phenyl H), 6.98 (m, 12H, phenyl H), 2.13 (m, 4H, CH₂). ³¹P NMR in CDCl₃: δ 40.9 (s).

[Et₄N][Ta(CO)₆]. [Et₄N][Ta(CO)₆] was synthesized by a variation of the method of Ellis *et al.*,^{10a} including the improvements outlined for the synthesis of [M(CO)₆]²⁻ (M = Ti, Zr, Hf).¹⁹ Naphthalene (13.0 g, 0.10 mol, excess) and sodium (1.5 g, 0.065 mol, cut into small pieces) were weighed into a flask,

and DME (150 mL) was added ([sodium naphthalenide] = 0.43 M). The mixture immediately turned green-black and was stirred at room temperature for 3 h to allow complete formation of the naphthalenide.

While the sodium naphthalenide was being formed, TaCl₅ (3.50 g, 9.77 mmol) was added slowly to 150 mL of rapidly stirred, cold (195 K) toluene. The sodium naphthalenide solution was cooled to 195 K and added to the white slurry of TaCl₅ in toluene to produce a dark-brown mixture. The flask was stirred at low temperature under CO for 6 to 8 h and then allowed to warm to room temperature overnight.

All subsequent manipulations were done under argon. [Et₄N]Br (3.00 g, 14.3 mmol) in water (50 mL) was slowly added to the reaction mixture over 30 min. Filtration of the brown slurry resulted in a bright orange-yellow solution and a brown tarry residue which were separated by filtration. The tar was washed with DME (5 × 20 mL), and the combined washings and filtrate were pumped down to remove DME and toluene. After most of the solvent was removed, 100 mL of water was added and the bright yellow precipitate was filtered out and dried. All naphthalene was removed by sublimation to give 1.2 g of product (26%). IR (THF): ν_{CO} 1888 (w, sh), 1859 cm⁻¹ (vs). Lit.^{10a} (THF, [(Ph₃P)₂N]⁺ salt): ν_{CO} 1882 (sh), 1854 cm⁻¹ (vs). Raman (powder): ν_{CO} 2024 (w), 1885 (vs), 1881 cm⁻¹ (vs).

[Et₄N][Ta(CO)₄(dppe)]. Method 1. [Et₄N][Ta(CO)₆] was substituted with dppe photolytically, according to the method of Davison and Ellis.^{10d} Photolysis was carried out using a 450 W Hanovia mercury vapor lamp, which was placed in a water-jacketed well in the reaction vessel. Dppe (1.70 g, 4.27 mmol) was weighed into a reaction vessel, and a solution of [Et₄N][Ta(CO)₆] (2.00 g, 4.17 mmol) in THF (100 mL) was added. The reaction vessel was placed on ice, and the sample was photolyzed for 4–6 h or until the carbonyl bands for the starting material had become very weak or had disappeared. The photolysis was monitored carefully since Davison and Ellis^{10d} report that the substituted anions of tantalum are easily decomposed by long exposure to UV radiation. Initially, carbonyl bands at 1968 (m) and 1822 (vs) cm⁻¹ were observed; these were tentatively attributed to the intermediate [Ta(CO)₅(dppe)]⁻ on the basis of literature data for [Ta(CO)₅PPh₃]⁻.^{10d} (A third band at ~1860 cm⁻¹ would be obscured by a band of the starting material.)

The reaction solution was filtered into a flask, and the precipitated orange-red solid was dried under vacuum and found to be pure [Et₄N][Ta(CO)₄(dppe)] by spectroscopic analysis. The photolysis apparatus was rinsed with acetonitrile (4 × 25 mL) to remove red solid adhering to the sides, and these acetonitrile washes were added to the filtrate. This solution was pumped dry at or below room temperature.

The solid recovered from the removal of the solvent consisted of [Et₄N][Ta(CO)₄(dppe)] plus small amounts of [Et₄N][Ta(CO)₅(dppe)] and free dppe. The solid was extracted into acetonitrile (3 × 10 mL) to remove a quantity of beige solid (dppe), and the extracts were pumped dry to yield a red-black, sticky material. Scraping this vigorously in the presence of pentane (discarding the pentane washes) allows a red solid to be recovered. The solid can be recrystallized from acetone, DME/hexanes, or from benzene/hexanes to yield red crystals of the product. Total yield: 1.75 g (51%).

Method 2. In an attempt to improve the overall yield of [Et₄N][Ta(CO)₄(dppe)], an adaptation of the method for the synthesis of [Et₄N][Ta(CO)₆] was attempted. A solution of dppe (3.90 g, 9.79 mmol) in 150 mL toluene was cooled to 195 K, and TaCl₅ (3.50 g, 9.77 mmol) was added slowly, producing a bright yellow suspension. A cold solution of sodium naphthalenide, prepared as above, was added to the suspension, producing a dark-brown mixture. The reaction was continued as described above for [Et₄N][Ta(CO)₆], warming to room temperature overnight.

All subsequent manipulations were done under argon. [Et₄N]Br (3.00 g, 14.3 mmol) was added to the dark slurry,

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which was stirred for 1 h and then filtered. (Water was not added to this reaction when the anion was the desired product because reaction results in formation of the hydride, TaH(CO)₄(dppe).) The brown, tarry residue was washed repeatedly with DME to give a dark red solution which was evaporated, at or below room temperature, to give crude, red product. Naphthalene was removed by sublimation.

In some cases the solid was found to consist of a mixture of the anions [Ta(CO)₆]⁻, [Ta(CO)₅(dppe)]⁻, and [Ta(CO)₄(dppe)]⁻; in general, photolysis of the solid (after sublimation of naphthalene) according to method 1 resulted in conversion to [Ta(CO)₄(dppe)]⁻ as the major product. In most cases, however, [Ta(CO)₄(dppe)]⁻ was essentially the only product, and purification as in method 1 was sufficient. Total yield: 2.4 g (30%). IR data in various solvents are given in Table 1. Raman (powder): ν_{CO} 1893 (vs), 1790 (w), 1779 (w), 1742 cm⁻¹ (m). ¹H NMR in CD₃CN: δ 7.69 (m, 8H, phenyl H), 7.27 (m, 12H, phenyl H), 3.14 (q, $J = 7.3$ Hz, 8H, CH₂ of [Et₄N]⁺), 2.37 (m, $J = 17.3$ Hz, 4H, CH₂ of dppe ligand), 1.19 (tt, $J = 1.8, 7.2$ Hz, 12H, Me of [Et₄N]⁺). ³¹P{¹H} NMR in CD₃CN: δ 49.2 (s). ³¹P{¹H} NMR in C₆D₆: δ 51.1 (s). Lit.²⁰ in THF/THF-*d*₈: δ 46.8 (s). ³¹P NMR of solid: δ 53.0 (s), 49.0 (s), 43.6 (s). ¹³C NMR of solid: δ 143.7 (s), 140.8 (s), 129.7 (s), 52.3 (s), 31.3 (br m), 7.9 (s).

TaH(CO)₄(dppe). TaH(CO)₄(dppe) was synthesized by variations of the method described by Rehder *et al.*²⁰

Method 1. A column of silica gel (Kieselgel 60, Merck) on glass frit (15 cm × 2.5 cm) was placed under dynamic vacuum for 1 to 2 h and then filled with first argon and then with acetonitrile. A saturated solution of [Et₄N][Ta(CO)₄(dppe)] (2.10 g, 2.56 mmol) in acetonitrile was then passed slowly through the column, and the colored solution which eluted was collected and pumped dry to yield a sticky red solid. Scraping the solid vigorously in the presence of pentane allowed isolation of TaH(CO)₄(dppe) as a powdery, pentane-soluble, reddish-brown solid. Yield: 1.20 g (68%).

Method 2. Method 2 for the synthesis of [Et₄N][Ta(CO)₄(dppe)] was followed through to warming to room temperature overnight under CO. Water (100 mL) was then added slowly to the solution, which was stirred at room temperature for 1 h. The resulting red solution was separated from a brown, tarry precipitate by filtering through a column of silica gel (~4 cm × 6 cm diameter). The column was thoroughly eluted with DME, and most of the solvent was removed under reduced pressure. More water (100 mL) was added, the precipitated solid was filtered out and pumped dry, and the reddish solid was chromatographed on silica gel (10–12 cm × 2 cm diameter) using hexanes, toluene, THF, and acetonitrile in that order. The initial colorless solution was discarded; all of the colored fraction was collected and pumped dry to yield reddish-brown, solid product.

The solid was extracted into acetonitrile (3 × 10 mL) and filtered to remove a quantity of yellow-beige solid. The deep-red extracts were pumped dry, and naphthalene was removed by sublimation. The acetonitrile extractions were repeated to remove more beige solid (3 × 5 mL), and the sticky red solid was stirred vigorously under pentane to obtain TaH(CO)₄(dppe) as a red-brown powder in 20–25% yield (1.35–1.70 g). IR data in various solvents are given in Table 2. Raman (powder): ν_{CO} 1986 (m), 1890 (m), 1862 (vs), 1694 cm⁻¹ (w). ¹H NMR in C₆D₆: δ 7.51 (m, 8H, phenyl H), 6.98 (m, 12H, phenyl H), 2.12 (m, $J = 18.2$ Hz, 4H, CH₂ of dppe), -2.61 (t, $J = 21.5$ Hz, 1H, TaH). ¹H NMR in CD₃CN: δ 7.43 (m, 12H, phenyl H), 7.23 (m, 8H, phenyl H), 2.67 (m, $J = 18.4$ Hz, 4H, CH₂ of dppe), -3.51 (t, $J = 19.9$ Hz, 1H, TaH). Lit.^{11c} in THF-*d*₈: δ -3.35 (t, 1H, $J = 21$ Hz). ³¹P{¹H} NMR in C₆D₆: δ 45.5 (s). ³¹P{¹H} NMR in CD₃CN: δ 43.9 (s). Lit.^{20a} in THF/THF-*d*₈: δ 43.3 (s). ³¹P NMR of solid: δ 64.1 (s, br), 44.3 (s, br), 27.2 (s, br). ¹³C NMR of solid: δ 129.3 (s), 23.3 (s).

Ta(CO)₄(dppe). In a typical synthesis, 100–150 mg of TaH(CO)₄(dppe) was dissolved in benzene (5 mL) and the solution was cooled to ~285 K. A solution of (*t*-BuC₆H₄)₃C⁺ (~1.0 molar equiv, based on 80% conversion from (*t*-BuC₆H₄)₃CBr) was added. There was an immediate color change from red to dark brown. After the solution was stirred for 15 min, the solvent was removed under vacuum. The resulting brown solid was washed with hexanes (3 × 10 mL) to remove organic compounds and dried under vacuum. When the reaction was carried out at temperatures greater than 285 K, the major product was TaBr(CO)₂(dppe)₂. The reaction was worked up under fluorescent lighting in order to decompose any excess (*t*-BuC₆H₄)₃C⁺ that might still be present.

Repeated attempts were made to recrystallize or to chromatograph the solid, but these were unsuccessful. The major product collected from the chromatography of Ta(CO)₄(dppe) on silica gel with toluene was TaH(CO)₄(dppe). The effects of a variety of solvents on Ta(CO)₄(dppe) are outlined below (with IR data). All attempted recrystallizations in benzene/hexanes or toluene/hexanes resulted in decomposition to a non-carbonyl-containing species and dppe. By following the procedure outlined above, Ta(CO)₄(dppe) was obtained relatively pure but was always contaminated with small amounts of dppe (from decomposition) and some organic species. Further purification was not possible.

Solid Ta(CO)₄(dppe) may be kept at 243 K for about 3 weeks. After this time, the complex shows signs of significant decomposition, as indicated by IR spectroscopy. Ta(CO)₄(dppe) was, therefore, only prepared as required and was used within 2 weeks of synthesis.

IR spectra were recorded in several solvents, and data are listed in Table 3. (Subtraction of benzene from the IR spectra is often a problem because of a band in the IR spectrum of benzene at ~1960 cm⁻¹; this coincides with one of the bands of Ta(CO)₄dppe and sometimes results in abnormal intensities for the 1960 cm⁻¹ band of Ta(CO)₄(dppe).) In toluene and benzene, Ta(CO)₄(dppe) was observed to decompose slowly (over a few hours) at/below 285 K. Above 285 K, the complex decomposed in about 1 h to a material which did not exhibit any carbonyl bands in the IR spectrum. In CH₂Cl₂, the complex decomposed faster, but it could be observed for at least 15 mins below 285 K; carbonyl bands attributable to TaH(CO)₄(dppe) and TaCl(CO)₄(dppe) were observed to grow in. IR spectra of Ta(CO)₄(dppe) could not be obtained in more polar solvents, although samples were taken immediately upon dissolving the solid. In diethyl ether, no carbonyl stretching bands were observed. The sample was pumped dry and redissolved in toluene. No carbonyl bands were observed, as the complex had completely decomposed to a non-carbonyl-containing species. In THF and acetonitrile, carbonyl bands for TaH(CO)₄(dppe) were observed in solution. Ta(CO)₄(dppe) apparently reacts with these solvents or with adventitious water.²¹

An IR spectrum was obtained of a toluene solution of Ta(CO)₄(dppe) at ~243 K, and carbonyl bands at 1962 (m), 1891 (s), 1878 (vs), and 1810 (w, br) cm⁻¹ were observed. NMR spectra of Ta(CO)₄(dppe) (saturated solution in C₆D₆) were recorded (~2000 scans) over the range δ 1100 to -1100. The spectrum was completely featureless except for two very broad resonances in the regions δ 0.5–3.5 and δ 6.7–8.2; lowering the temperature to 213 K had little effect on band widths.

A sample of Ta(CO)₄(dppe) was prepared in toluene-*d*₈, and ³¹P NMR spectra were collected over the temperature range 298–190 K. As the temperature decreased, a very broad (~75 ppm) resonance centered at ~ δ 48 appeared at ~233 K. The solid-state MAS ³¹P NMR spectrum exhibited resonances at δ 85.0 (s, br), 60.2 (s, br), 33.6 (s, br), and 15.7 (s, br).

Magnetic Susceptibility. Evans' NMR method¹⁶ for the determination of the paramagnetism of a compound in solution

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was used to characterize Ta(CO)₄(dppe). In all experiments, Ta(CO)₄(dppe) was prepared by reaction of TaH(CO)₄(dppe) with a deficiency of (*t*-BuC₆H₄)₃C⁺. After 15 min, the solvent was removed under reduced pressure and the solid residue was dissolved in C₆D₆ (or toluene-*d*₆) containing mesitylene and cyclohexane (1–5% v/v each) as susceptibility shift resonances. Portions of this solution were placed in two 5 mm NMR tubes, one of which was used to collect a reference spectrum. A sample of the solvent mixture was placed in a 3 mm tube to a depth of 3 cm, and this tube was then lowered into the second 5 mm NMR tube containing TaH(CO)₄(dppe) sufficiently carefully that no mixing of the two solutions occurred. Spectra were collected at room temperature and at temperatures in the range 213–298 K (toluene-*d*₆), concentrations being calculated by making solvent density corrections.^{16d} No precipitates were observed in the samples studied at low temperature.

Using a Johnson Matthey magnetic susceptibility balance, the solid Ta(CO)₄(dppe) was found to be diamagnetic ($\chi_g = -3.1 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$).

EPR Spectroscopy. No EPR signal was observed for either a solid sample or a toluene solution of Ta(CO)₄(dppe) at 11 or 223 K. To ensure that the solution sample had not decomposed, an NMR sample of the material was subsequently prepared and shown to be paramagnetic using the Evans method ($\mu \approx 1.6 \mu_B$).

Reactions of Tantalum Complexes with Organic Halides. The compounds [Et₄N][Ta(CO)₄(dppe)] (at 295 K), Ta(CO)₄(dppe) (below 285 K), and TaH(CO)₄(dppe) (at 295 K) (10–15 mg in 3–5 mL of toluene or 1–1.5 mL of toluene-*d*₆) were reacted with allyl bromide, benzyl bromide, methyl iodide, ethyl iodide, isopropyl iodide, *tert*-butyl iodide, CCl₄, and (*t*-BuC₆H₄)₃CBr (2–10-fold molar excess), the reactions being monitored by IR and/or ¹H NMR spectroscopy. Spectra of reaction mixtures were generally collected within 5 min, and in some cases, reactions were monitored for up to 1 h.

Results and Discussion

Syntheses of [Ta(CO)₆]⁻, [Ta(CO)₄(dppe)]⁻, and TaH(CO)₄(dppe). Two general procedures have been reported for the synthesis of [Ta(CO)₆]⁻. In the first, using magnesium and zinc in pyridine (eq 2), the reaction must be heated to 85 °C under a pressure of 10 atm of carbon monoxide in order to achieve a reasonable rate of reaction, and a yield of ~35% of [Ta(CO)₆]⁻ as a solvated sodium salt is obtained.^{10a} In the second, using alkali metal naphthalenides as reducing agents (eq 4), high pressures of carbon monoxide are not required, and yields as high as 53% have been reported.^{10b,e}

The lithium naphthalenide reduction procedure was therefore chosen for this work, and yields of ~15% were obtained. Although these yields do not correspond to the reported yield, our results are in agreement with those of Rehder *et al.*,²² who obtained yields of 15% using lithium naphthalenide. Following a later report by Ellis *et al.*¹⁹ for the synthesis of [M(CO)₆]²⁻ (M = Ti, Zr, Hf), we used sodium naphthalenide. Yields were improved, albeit only to ~20%, by maintaining the reactions under a blanket of CO rather than by bubbling CO through the reaction mixture.

One of the difficulties with this preparation is that TaCl₅ forms an unidentified byproduct if it is added too quickly to DME (even at -78 °C).^{10b} However, solutions of TaCl₅ in toluene (or benzene) have apparently been

obtained at room temperature,^{13b,23} and using toluene as solvent for the TaCl₅, yields were improved to ~26%. Additional changes made to optimize the yield are described in the Experimental Section. In all cases, the reactions were carried out using glass-covered stir bars and stainless steel cannulas because alkali metal naphthalenides reportedly react with Teflon.¹⁹

Although Calderazzo *et al.*^{11c} reported a one-pot synthesis of TaH(CO)₄(dppe), involving the slow addition of HCl to a toluene solution of [Et₄N][Ta(CO)₆] and dppe at 195 K, we were unable to duplicate their method. Using this approach, the only products we observed by IR spectroscopy were TaCl(CO)₄(dppe) and TaCl(CO)₂(dppe)₂, although much of the starting material decomposed to non-carbonyl-containing complexes. In order to attempt to avoid formation of the chloro species, other proton acids were also tried, but the hydride was not obtained; decomposition was usually observed.

A previously reported two-step approach was therefore chosen. In this method, the dppe-substituted anion was synthesized first, followed by protonation to form the desired hydride. Photolysis of [Et₄N][Ta(CO)₆] in the presence of dppe was found to proceed in ~50% yield, as described by Davison and Ellis.^{10d} Rehder *et al.*^{20a} reported obtaining yields of 84% for this complex (over a shorter period of time) but apparently with different equipment.^{10d}

Although Davison and Ellis^{10d} report that no mono-substituted anion was observed during photolysis of the niobium or tantalum hexacarbonylates in the presence of dppe, we did observe an apparent monosubstituted intermediate by IR spectroscopy. With carbonyl bands at 1968 (m) and 1822 (vs) cm⁻¹ in THF, the spectrum of the species compared favorably with that of [Et₄N][Ta(CO)₅PPh₃] (ν_{CO} (THF) 1973 (s), 1863 (m) and 1828 (vs) cm⁻¹).^{10d} The third band (~1860 cm⁻¹) would be obscured by the major carbonyl band for the hexacarbonylate (1859 cm⁻¹ in THF).

In several reports, TaCl₅ has been reduced in the presence of phosphine ligands, giving substituted complexes which can then be reductively carbonylated.^{13b} In addition, Rehder *et al.* reported the synthesis of NbCl(CO)₃(bdpm) (bdpm = MeP(CH₂CH₂CH₂PMe₂)₂) from the reaction of NbCl₄(THF)₂ with bdpm and CO under reducing conditions.^{24a} Ellis *et al.*^{24b} report that PME₃ was required for the reductive carbonylation of MCl₄·THF (M = Zr, Hf) with sodium naphthalenide. Apparently the phosphine stabilized an intermediate species, although the phosphine was not present in the isolated complex.^{24b} However, the substituted complexes M(CO)₄(trmpe) (M = Ti, Zr, Hf; trmpe = MeC(CH₂PMe₂)₃) were isolated from a similar reductive carbonylation,^{24c} and this procedure was therefore attempted with dppe and TaCl₅.

Substitution and carbonylation of TaCl₅ did, in fact, occur in the presence of dppe, and the yields of the substituted anion by this method were 30%, a definite

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Table 1. IR Data for [Et₄N][Ta(CO)₄(dppe)]

solvent	ν_{CO} (cm ⁻¹)
acetonitrile	1904 (s), 1786 (vs), 1755 (m, sh)
CH ₂ Cl ₂	1903 (m), 1790 (vs), 1772 (s, sh), 1742 (m, br)
THF	1906 (m), 1799 (vs), 1779 (m), 1750 (m); lit. (THF) 1908 (s), 1800 (vs), 1779 (s), 1752 (m) ^{10d}
toluene	1893 (m), 1789 (m), 1756 (m), 1735 (vs); lit. (Nujol) 1893 (s), 1778 (s), 1755 (s), 1736 (vs) ^{10d}

improvement over the previous results. It should be noted, however, that all manipulations had to be carried out at or below room temperature during the workup of this reaction because [Et₄N][Ta(CO)₄(dppe)] is extremely thermally labile. As well, [Et₄N]Br cannot be added as an aqueous solution when the substituted anionic complex is the desired product because the latter reacts with water to form the hydride. However, while mixtures of the anions [Ta(CO)₆]⁻, [Ta(CO)₅(dppe)]⁻, and [Ta(CO)₄(dppe)]⁻ were occasionally obtained, photolysis of the recovered solids (after sublimation of naphthalene) always resulted in overall conversion to the desired [Ta(CO)₄(dppe)]⁻. In most cases [Ta(CO)₄(dppe)]⁻ was essentially the only product. IR spectral data for [Et₄N][Ta(CO)₄(dppe)] in various media are listed in Table 1. As can be seen, the carbonyl stretching bands are generally very broad and the positions of the bands vary significantly with the solvent.

The method of Rehder *et al.*²⁰ was chosen for the synthesis of the hydride from [Et₄N][Ta(CO)₄(dppe)]. By eluting the substituted anion through silica gel, the authors reported yields of the hydride of 84%;^{20a} we have obtained 68%. Other methods of protonation of [Ta(CO)₄(dppe)]⁻ have been reported,^{6d} but use of a column of silica gel generally results in the synthesis of the hydride free of all reagents used for its synthesis except dppe; some dppe is always found in the eluted solution. Using the original three-step synthesis, the overall yield of the hydride was 5–9%. By synthesis of [Et₄N][Ta(CO)₄(dppe)] directly from TaCl₅, overall yields were three to four times higher (~20%).

In an attempt to further improve yields of the hydride, a reaction mixture produced by carbonylation of TaCl₅ in the presence of dppe was eluted directly through silica gel; the yield of hydride was now 20–25%. For the synthesis of substituted hydride complexes, this method represents a significant decrease in the number of manipulations and in the time required. However, there was little improvement in yield when Na[Ta(CO)₄(dppe)] was chromatographed directly as compared to purifying [Et₄N][Ta(CO)₄(dppe)] first. However, it is easier to purify the hydride than the anionic complex because the hydride is, perhaps surprisingly, less sensitive to temperature.

Infrared spectra were collected in a variety of solvents, and the carbonyl stretching frequencies are reported in Table 2. The hydride presumably assumes a distorted pentagonal bipyramid structure, as observed for the analogous vanadium hydride,²⁵ but is probably stereochemically nonrigid. Indeed, observation of five carbonyl stretching bands in most solvents suggest that more than one geometric isomer exists in solution. As with [Et₄N][Ta(CO)₄(dppe)], the carbonyl stretching bands are generally broad and the frequencies are

Table 2. IR Data for TaH(CO)₄(dppe)

solvent/medium	ν_{CO} (cm ⁻¹)
Nujol	1987 (m), 1896 (vs), 1879 (vs), 1844 (vs); lit. 1990 (m), 1865 (vs, br) ^{20a}
hexanes	2008 (m), 2001 (m), 1929 (m), 1906 (m), 1870 (vs)
benzene, toluene	2004 (m), 1997 (m), 1914 (s), 1894 (s), 1866 (vs); lit. (toluene) 1994 (m), 1911 (sh), 1892 (s), 1863 (vs) ^{11c}
CH ₂ Cl ₂	2002 (m), 1998 (m), 1907 (m), 1885 (s), 1864 (vs)
ethyl ether	2004 (m), 1999 (m), 1917 (s), 1898 (s), 1870 (vs)
THF, acetonitrile	2001 (m), 1996 (m), 1906 (m, sh), 1889 (s, sh), 1869 (vs, br); lit. (THF) 1998 (m), 1860 (vs, br) ^{11c}

Table 3. IR Data for Ta(CO)₄(dppe)

solvent	ν_{CO} (cm ⁻¹)
Nujol	1958 (m), 1870 (vs, br), 1830 (m, sh), 1793 (m)
benzene	1960 (w), 1892 (s), 1877 (vs)
toluene	1962 (m), 1891 (s), 1878 (vs)
CH ₂ Cl ₂	1962 (w), 1870 (vs, br)

strongly solvent dependent. Moreover, the spectra obtained are different from some reported in the literature (Table 2). However, once we had fully assessed the chemical behavior of the hydride in the various solvents and had learned how to purify and work with it, completely consistent spectra of this compound were obtained over several years. Moreover, the spectra of all possible carbonyl-containing impurities are also now recognizable, and we have confidence in the accuracy of the data in Table 2.

Synthesis of Ta(CO)₄(dppe) via Hydride Atom Abstraction Using (*t*-BuC₆H₄)₃C•. Eisenberg *et al.*^{15c} reported the generation of (*t*-BuC₆H₄)₃C• from (*t*-BuC₆H₄)₃CBr in a variety of solvents, using several metal reducing reagents and at several temperatures. In order to obtain the best possible conversion of (*t*-BuC₆H₄)₃CBr to Ta(CO)₄(dppe), a variety of reaction conditions were assessed, the processes being monitored by UV–vis spectroscopy (for the radical, $\lambda_{\text{max}} = 524$ nm, $\epsilon = 825$ M⁻¹ cm⁻¹).^{15c} Note that sensitivity of the radical to room light necessitated all manipulations being carefully carried out in the absence of light. Although Eisenberg *et al.*^{15c} reported the successful manipulation of the radical in THF, we found that solutions in THF decompose rapidly. In contrast, solutions of the radical in benzene or toluene are reasonably stable for a few minutes, during manipulations and on exposure to adventitious light.

An instantaneous color change from red to dark brown was noted when a solution of TaH(CO)₄(dppe) in toluene or benzene at room temperature was treated with a solution of (*t*-BuC₆H₄)₃C•; the 17-electron compound Ta(CO)₄(dppe) was formed. Monitoring by IR spectroscopy showed that the reaction was complete by the time a spectrum could be collected, although the reaction solution was stirred for a further 10 min in the light in order to decompose any unreacted (*t*-BuC₆H₄)₃C•. The product was isolated by removing the solvent under reduced pressure followed by extraction of organic (trityl-containing) byproducts with hexanes.

Ta(CO)₄(dppe) was found to be thermally very unstable in a variety of solvents. Thus decomposition occurred during all attempts to recrystallize Ta(CO)₄(dppe), and uncoordinated dppe was found to contami-

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Table 4. Comparative IR and Raman Data for Ta(CO)₄(dppe) and Related Complexes

conditions	complex	ν_{CO} (cm ⁻¹)
IR (toluene)	[Et ₄ N][Ta(CO) ₄ (dppe)]	1893 (m), 1789 (m), 1756 (m), 1735 (vs)
	TaH(CO) ₄ (dppe)	2004 (m), 1997 (m), 1914 (s), 1894 (s), 1866 (vs)
	Ta(CO) ₄ (dppe)	1962 (m), 1891 (s), 1878 (vs)
	TaBr(CO) ₄ (dppe) ^{11c}	2024 (s), 1950 (m), 1903 (vs), 1881 (s) ^{11c,32}
	W(CO) ₄ (dppe)	2017 (m), 1917 (s), 1904 (vs), 1887 (s)
IR (toluene, 243 K)	Ta(CO) ₄ (dppe)	1962 (m), 1891 (s), 1878 (vs), 1810 (w, br)
	TaH(CO) ₄ (dppe)	1987 (m), 1896 (vs), 1879 (vs), 1844 (vs)
	HV(CO) ₄ (dppe) ^{6d}	1988 (m), 1890 (vs), 1867 (vs, sh), 1856 (vs)
	V(CO) ₄ (dppe) ^{6d}	1985 (s), 1889 (s), 1870 (vs), 1849 (vs)
IR (Nujol mull)	[Et ₄ N][Ta(CO) ₄ (dppe)]	1893 (vs), 1790 (w), 1779 (w), 1742 (m)
	TaH(CO) ₄ (dppe)	1986 (m), 1890 (m), 1862 (vs), 1694 (w)
	W(CO) ₄ (dppe)	2013 (s), 1901 (vs), 1854 (vs)
Raman (powder)	Ta(CO) ₄ (dppe)	1960 (vs), 1881 (s), 1823 (m), 1812 (m, sh), 1799 (w, sh)

nate all solid materials obtained. Solid Ta(CO)₄(dppe) was even found to decompose at 243 K over a few weeks under a nitrogen atmosphere, and thus, it was not possible to obtain pure material for elemental analyses. The characterization of Ta(CO)₄(dppe), while very involved and complicated, was nevertheless unambiguously achieved through a combination of spectroscopic and chemical studies.

The monomeric compound Ta(CO)₄(dppe) should assume essentially a *cis*-octahedral structure (*C*_{2v}), giving rise to four carbonyl stretching bands (2a₁ + b₁ + b₂), all of which are IR and Raman active.²⁶ Moreover, the IR spectrum should exhibit a characteristic pattern of intensities, *i.e.* a sharp, medium-intensity, high-frequency a₁ mode and, to lower frequencies, medium to strong a₁, b₁, and b₂ modes, possibly overlapping.²⁶ Solution IR spectra of Ta(CO)₄(dppe) (Table 3) in toluene and benzene exhibited three carbonyl bands, a relatively narrow band at ~1960 cm⁻¹ and two stronger, overlapping bands at lower frequencies. Since the two lower frequency bands are sufficiently broad that either could obscure a fourth band, the spectra are indeed compatible with the suggested structure; unfortunately, low solubilities precluded the acquisition of a solution Raman spectrum.

Comparisons of the IR solution spectra of Ta(CO)₄(dppe) with the carbonyl stretching data of other compounds in Table 4 are very useful. The carbonyl stretching bands of Ta(CO)₄(dppe) lie to lower frequencies than those of the parent hydride, the differences being greater than is observed between HV(CO)₄(dppe) and V(CO)₄(dppe).^{6d} The carbonyl stretching bands of Ta(CO)₄(dppe) also lie to lower frequencies than those of the tungsten analogue, W(CO)₄(dppe), surprisingly implying a greater degree of back-donation in the d⁵ system, but are comparable in frequency to those of the vanadium analogue, V(CO)₄(dppe).^{6d} We note that the IR spectrum of the putative Ta(CO)₆, formed by cocondensing tantalum atoms and CO molecules in an argon matrix at ~4 K, exhibits a carbonyl stretching band (1967 cm⁻¹)^{7a} which lies to significantly lower frequency than does the corresponding band of solid W(CO)₆ (~1982 cm⁻¹).^{7b} The spectra of TaH(CO)₄(dppe), Ta(CO)₄(dppe), and W(CO)₄(dppe) are illustrated for purposes of comparison in Figure 1.

The Nujol mull IR spectrum of Ta(CO)₄(dppe) is very different from the solution spectrum, at least two bands in the bridging carbonyl region, 1795–1830 cm⁻¹, being

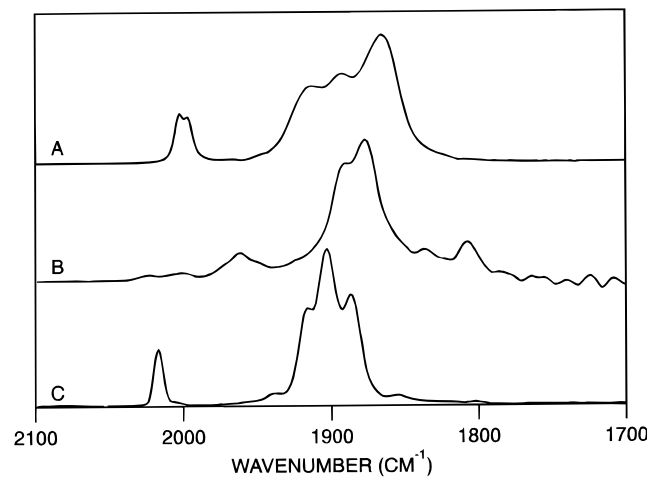


Figure 1. IR spectra of TaH(CO)₄(dppe) (A), Ta(CO)₄(dppe) (B), and W(CO)₄(dppe) (C).

observed in addition to differences in the terminal carbonyl region. It is thus apparent that the new tantalum(0) system assumes different structures in the solid state and in solution. A low-temperature (243 K) solution IR spectrum of Ta(CO)₄(dppe) exhibits a weak band at 1810 cm⁻¹ in addition to the bands observed in the room-temperature spectrum, and we conclude that the monomeric Ta(CO)₄(dppe) is the dominant species in solution over a wide range of temperature but that it exists in solution in equilibrium with the dimer, [Ta(CO)₄(dppe)]₂, which contains at least two bridging carbonyl groups. The compound assumes only the carbonyl-bridged dimeric structure in the solid state, and thus the tantalum compound stands in strong contrast to the vanadium system, where dimerization does not occur.^{1,2,6a}

Consistent with these results, the tantalum(0) system is EPR silent both in the solid state, where it probably exists as a metal–metal-bonded diamagnetic dimer, and in solution, where it apparently undergoes severe broadening because of facile monomer–dimer exchange. Similar results have been found previously for the chromium-centered radicals, CpCr(CO)₃ and Cp*Cr(CO)₃, the EPR spectra of which could only be observed on samples doped into diamagnetic matrices.²⁷ Unfortunately, all attempts to dope Ta(CO)₄(dppe) into crystals

(27) (a) Morton, J. R.; Preston, K. F.; Cooley, N. A.; Baird, M. C.; Krusic, P. J.; McLain, S. J. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3535. (b) Cooley, N. A.; Baird, M. C.; Morton, J. R.; Preston, K. F.; LePage, Y. *J. Magn. Reson.* **1988**, *76*, 325. (c) Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Fortier, S.; Watson, K. A.; Hensel, K.; Baird, M. C.; Preston, K. F.; Morton, J. R.; LePage, Y.; Charland, J.-P.; Williams, A. J.; Ziegler, T. *J. Am. Chem. Soc.* **1991**, *113*, 542.

(26) Adams, D. M. *Metal-Ligand and Related Vibrations*; Edward Arnold Publishers: London, 1967; p 100.

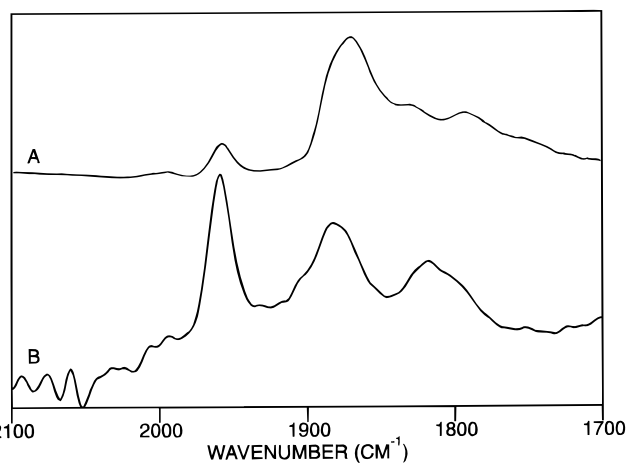


Figure 2. IR (A) and Raman (B) spectra of Ta(CO)₄(dppe) (both in Nujol).

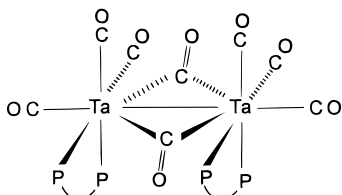


Figure 3. Suggested structure for [Ta(CO)₄(dppe)]₂.

the 18-electron tungsten analogue, W(CO)₄(dppe), failed because of the low thermal stability of the tantalum compound.

Also consistent with facile equilibration between a diamagnetic dimer and a paramagnetic monomer, a room-temperature ¹H NMR spectrum exhibited only extremely broadened resonances at δ 0.5–3.5 and δ 7–8.2, presumably corresponding to the methylene and phenyl protons, respectively. The ³¹P NMR spectrum at 298 K exhibited no resonances except for those of free dppe and some minor impurities, but as the temperature was lowered, a very broad (~75 ppm) resonance centered at ~δ 48 appeared below ~233 K. The solid-state ³¹P NMR spectrum exhibited resonances of comparable chemical shifts at δ 85.0 (s, br), 60.2 (s, br), 33.6 (s, br), and 15.7 (s, br), and these are undoubtedly to be attributed to the dimer, [Ta(CO)₄(dppe)]₂. The multiplet pattern in the ³¹P spectrum in the solid state presumably arises from dipolar interactions with the ¹⁸¹Ta nucleus (*I* = 7/2),²⁸ but such effects are normally impossible to observe in solution because of the efficiency of the quadrupolar relaxation mechanism.

The Raman spectrum (Nujol) of the solid material, illustrated in Figure 2, also exhibits two terminal and two bridging carbonyl stretching bands, with frequencies very similar to those in the IR spectrum. Thus it seems likely that the dimer is of low symmetry and is certainly not centrosymmetric. A reasonable structure for [Ta(CO)₄(dppe)]₂, compatible with the spectroscopic data, is shown in Figure 3.

Attempts to obtain solution IR spectra of Ta(CO)₄(dppe) in other than aromatic solvents provided some interesting observations on the reactivity of this compound. The hydride, TaH(CO)₄(dppe), was formed in THF and acetonitrile, but dissolving in ethyl ether

resulted in decomposition to non-carbonyl-containing species and the reactions were not investigated further.

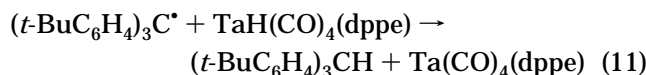
Magnetic Susceptibility Measurements on Ta(CO)₄(dppe). The Evans NMR method^{16a–c} was used to determine the magnetic susceptibility of Ta(CO)₄(dppe) in solution. For NMR samples prepared by utilizing two concentric tubes as described in the Experimental Section, the mass susceptibility of the solute, χ_g, is given by eq 10,^{16a–c} where χ₀ is the mass

$$\chi_g = \chi_0 + 3000\Delta\nu/4\pi\nu_0cM + \chi_0(d_0 + d_s)/c \quad (10)$$

susceptibility of the pure solvent, Δν is the change in frequency (or susceptibility shift, in Hz) of the resonances of inert species in solution (cyclohexane, mesitylene), ν₀ is the spectrometer frequency (400 MHz), *c* is the concentration of the paramagnetic substance in mol L⁻¹, and *M* is its molecular weight in g mol⁻¹. The third term of eq 10 is a correction term to account for the difference in density of the pure solvent, *d*₀, and the solution, *d*_s; this term is generally very small for highly paramagnetic samples and was neglected, as usual.^{16a–c,29a}

The Evans NMR method has proven to be very useful for the characterization of Ta(CO)₄(dppe) even though the compound cannot be purified. As outlined in the Experimental Section, hydrogen abstraction reactions were carried out using slight excesses of TaH(CO)₄(dppe) so that residual resonances for the hydride could be observed in the reference spectrum. In particular, the presence of the high-field hydride resonances was used for identification since it was well-separated from any other resonances in the ¹H NMR spectra. With excess hydride compound present in solution, there would not be any (*t*-BuC₆H₄)₃C[•] remaining and thus any paramagnetism must be due to tantalum species present. As well, (*t*-BuC₆H₄)₃CH was observed in the NMR spectrum, the tertiary CH resonance being characteristic and well shifted away from all other resonances.

Concentrations of Ta(CO)₄(dppe) in the reaction mixtures were calculated as follows. From the reference spectrum prepared as described in the Experimental Section, the methyl resonances of (*t*-BuC₆H₄)₃CH were integrated relative to the total methyl resonances for these species present (including species formed from decomposition). This allowed the calculation of the concentration of (*t*-BuC₆H₄)₃CH from the total number of moles of (*t*-BuC₆H₄)₃CBr added. On the basis of the stoichiometry of the reaction of eq 11, the concentration of Ta(CO)₄(dppe) was then calculated.



Measurements of the susceptibility shifts in the temperature range 213–298 K were all made in duplicate, and the mass susceptibilities, corrected for changes to the solvent density at the temperatures studied, were calculated as in eq 10. The changes in χ_g as a function

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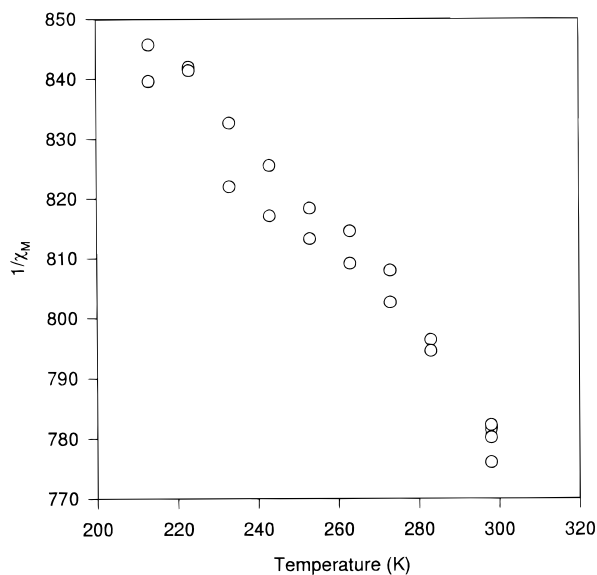


Figure 4. Plot of $1/\chi_M$ vs T .

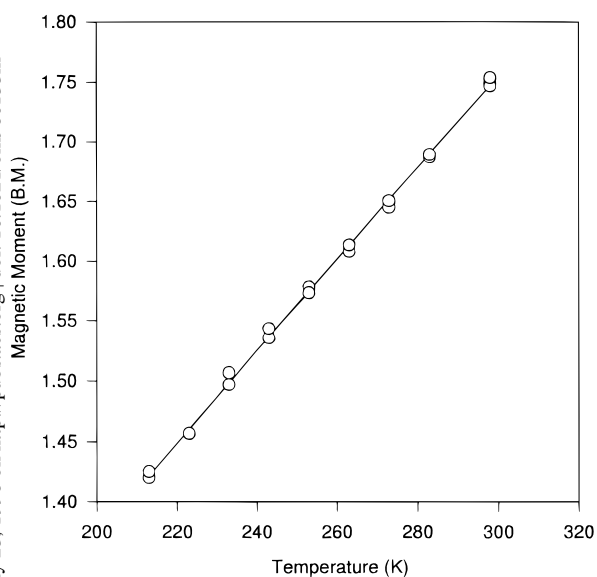


Figure 5. Plot of μ vs T .

of temperature were found to be completely reversible, and the results of the two experiments are in very close agreement. The molar susceptibilities, χ_M , were calculated and corrected for the diamagnetic effects of the ligands about the metal center in the usual way.^{16,27} The magnetic moments μ (μ_B) were determined^{29a,b} and, for samples measured at room temperature, were found to be very close to the value for one unpaired electron (1.73 μ_B).^{16,29}

The magnetic susceptibility of a magnetically dilute, paramagnetic compound generally decreases as the temperature increases, thus exhibiting Curie law behavior^{29a,d} as in eq 12. Here C is the Curie constant

$$\chi_M = C/T \quad (12)$$

and is a characteristic of the compound.^{29a,d} A plot of $1/\chi_M$ vs T should result in a straight line, and the magnetic moment should be independent of temperature.^{29a} However, a plot of $1/\chi_M$ vs T (Figure 4) is a curve and a plot of μ vs T (Figure 5) is a straight line, with the magnetic moment decreasing significantly as the temperature decreases. The mass susceptibility

of a 63 mg sample of solid $\text{Ta}(\text{CO})_4(\text{dppe})$ was also determined using a Johnson Matthey magnetic susceptibility balance; the material was found to be diamagnetic ($\chi_g = -3.1 \times 10^{-8} \text{ cm}^3 \text{ g}^{-1}$).

The solution magnetic susceptibility results are completely compatible with dimerization of $\text{Ta}(\text{CO})_4(\text{dppe})$ to $[\text{Ta}(\text{CO})_4(\text{dppe})]_2$ at low temperatures, through metal-metal bond formation. The results are quite also consistent with the observation of diamagnetism for the solid compound and with our observations that the solution and solid state IR and Raman spectra are different. Assuming monomer and dimer magnetic moments of 1.73 and 0 μ_B , respectively, an equilibrium constant for the monomer-dimer equilibrium was calculated from the solution magnetic susceptibility data. The theoretical molar susceptibility of a paramagnetic species in solution at temperature T can be calculated from eq 13, where μ_0 is 1.73.^{29a} The concentration

$$\chi_{\text{rad}} = \frac{N(\mu_0)^2 \beta^2}{3kT} \quad (13)$$

obtained from eq 11 represents the total tantalum concentration (monomer plus dimer), and the molar susceptibility calculated from this value represents the total susceptibility of the sample. Since the mass susceptibility (eq 10) and hence the molar susceptibility varies as the inverse of the concentration, the concentration of the radical can be calculated as

$$[\text{Ta}(\text{CO})_4(\text{dppe})] = [\text{total Ta}] \frac{\chi_{\text{total}}}{\chi_{\text{rad}}} \quad (14)$$

and the equilibrium constant is given by

$$K = \frac{[\text{Ta}(\text{CO})_4(\text{dppe})]^2}{[\text{dimer}]} \quad (15)$$

where

$$[\text{dimer}] = \frac{[\text{total Ta}] - [\text{Ta}(\text{CO})_4(\text{dppe})]}{2} \quad (16)$$

From a plot of $\ln K$ vs $1/T$ (Figure 6; deviation from linearity at the lowest temperature, where $\Delta\nu$ is at a minimum, probably reflects experimental error), ΔH , ΔS , and ΔG ²¹³ for the dissociation of the dimer were calculated to be 4.0 kcal mol⁻¹, 12 cal mol⁻¹ K⁻¹, and 1.4 kcal mol⁻¹, respectively. While the enthalpy of dissociation is significantly less than those of the dimeric compounds $[\text{CpCr}(\text{CO})_3]_2$ and $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2$, which also dissociate significantly in solution,³⁰ our observation that dimerization occurs at all with $\text{Ta}(\text{CO})_4(\text{dppe})$ is in strong contrast to the findings for vanadium(0) 17-electron complexes, which exist solely as paramagnetic monomers.^{1,2} However, metal-metal bonds of the 5d metals are generally much stronger than those of the 3d analogues.³¹

Reactions of $\text{Ta}(\text{CO})_4(\text{dppe})$ with Organic Halides. A reaction which is characteristic of 17-electron,

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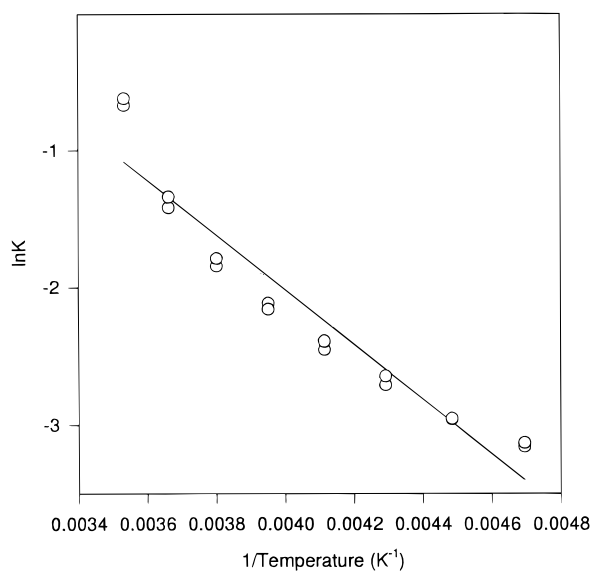


Figure 6. Plot of $\ln K$ vs $1/T$.

metal-centered radicals is the abstraction of halogen atoms from alkyl halides (eq 17).¹ When L_nM^* is present



at sufficiently high concentrations that bimolecular coupling reactions of L_nM^* and R^* become competitive, the corresponding alkylmetal compounds L_nMR may also be formed. Then the net overall reaction is



In such cases, the rates of reaction increase as the strength of the R-X bond decreases, *i.e.* $I > Br > Cl$, $t\text{-Bu} > i\text{-Pr} > Et > Me$; benzylic and allylic halides also react relatively quickly.

In the case of Ta(CO)₄(dppe), reactions as in eq 17 would yield as primary products the halo species Ta(CO)₄(dppe)X, which have been reported;^{11c} in the presence of free dppe, which is always present in solutions of Ta(CO)₄(dppe), conversion to Ta(CO)₂(dppe)₂X occurs slowly. Well-characterized organotantalum compounds of the type Ta(CO)₄(dppe)R have not been reported, although compounds of the type Ta(CO)₂(dppe)₂R are known.^{13b}

Accordingly solutions of Ta(CO)₄(dppe) (toluene for IR, C₆D₆ or toluene-*d*₈ for ¹H NMR studies) were reacted with carbon tetrachloride, allyl, benzyl, and tris(*tert*-butyl-phenyl) bromide, and methyl, ethyl, isopropyl, and *tert*-butyl iodide. For purposes of comparison and to ensure that any reactions observed were not a result of adventitious TaH(CO)₄(dppe) or [Et₄N][Ta(CO)₄(dppe)], these complexes were also treated with the same organic halides. It should be noted that the latter is sufficiently soluble in benzene and toluene that useful IR and ¹H NMR spectra could be obtained in these solvents.

Reactions of CCl₄ with TaH(CO)₄(dppe) and Ta(CO)₄(dppe) in toluene both proceeded very rapidly to give TaCl(CO)₄(dppe) (ν_{CO} 2024 (s), 1956 (m), 1902 (vs), and 1885 (m) cm⁻¹) and TaCl(CO)₂(dppe)₂ (ν_{CO} 1837 (m) and 1762 (w) cm⁻¹), identified by IR^{11c,32} and ¹H NMR spectroscopy. This perhaps inconclusive result is not

surprising for the hydride, as transition metal hydrides are often chlorinated by CCl₄.

Reactions with the homologous series of four alkyl iodides in toluene were rather more informative, as Ta(CO)₄(dppe) reacted very slowly with MeI (weak carbonyl bands for TaI(CO)₄(dppe)^{11c,32} at 2023 (m), 1978 (m), 1904 (vs), and 1880 (m) cm⁻¹ after 45 min), somewhat less slowly with EtI (weak carbonyl bands for TaI(CO)₄(dppe) after 15 min, medium-intensity bands after 1 h), much faster with *i*-PrI (medium-intensity carbonyl bands for TaI(CO)₄(dppe) after 5 min), and very rapidly for *t*-BuI (conversion to TaI(CO)₄(dppe) complete within 1 min). In some spectra, weak bands attributable to TaI(CO)₂(dppe)₂ were observed at 1837 (vs) and 1764 (m, br) cm⁻¹.

The reactions of MeI, EtI, and *i*-PrI were too slow for ¹H NMR spectroscopy to be useful. In all cases, decomposition to non-carbonyl-containing materials was significant and the carbonyl bands for the probable iodo products are sufficiently broad that their identification in low concentrations is not possible. In addition, ¹H NMR resonances of the iodo products are all sufficiently broad that identification of low concentrations is not feasible. Reactions of *t*-BuI with TaH(CO)₄(dppe) and [Et₄N][Ta(CO)₄(dppe)] were very slow.

Reaction of Ta(CO)₄(dppe) with allyl bromide in toluene was completed within 1 min, the strong carbonyl bands of TaBr(CO)₄(dppe) (2024 (s), 1950 (m), 1903 (vs), and 1881 (s) cm⁻¹)^{11c,32} being observed. In addition, weaker carbonyl bands of TaBr(CO)₂(dppe)₂ (1838 (vs) and 1761 (m) cm⁻¹)³² were also present. Interestingly, monitoring of the reaction by ¹H NMR spectroscopy revealed both the resonances of TaBr(CO)₄(dppe)³² and a set of resonances which seem attributable to the new compound $\eta^1\text{-C}_3\text{H}_5\text{Ta}(\text{CO})_4(\text{dppe})$ (¹H NMR in toluene-*d*₈: δ 3.43 (d, $J = 6.6$ Hz), 4.87 (d, $J = 10$ Hz), 5.02 (d, $J = 17$ Hz), 5.83 (m)). No apparent reaction of allyl bromide with TaH(CO)₄(dppe) or [Et₄N][Ta(CO)₄(dppe)] was observed after 5 min, although very weak bands corresponding to TaBr(CO)₄(dppe) could be observed after 35 min.

The reaction of Ta(CO)₄(dppe) with benzyl bromide in toluene was complete within ~ 1 min, and again TaBr(CO)₄(dppe) and TaBr(CO)₂(dppe)₂ were observed (IR).^{11c,32} In an NMR experiment, weak resonances of the bromo complex were observed in the phenyl region; the resonance at δ 6.80 is well separated from the rest of the phenyl resonances in the spectrum³² and was used to identify the bromo complex in the spectrum (because of the breadth of the CH₂ resonances, they are difficult to observe when only a small quantity of the complex is present).³² As well, a new singlet was observed at δ 4.05 (in toluene-*d*₈); this singlet is downfield of the singlet for benzyl bromide at δ 3.95 and is tentatively attributed to the benzyltantalum complex PhCH₂Ta(CO)₄(dppe).

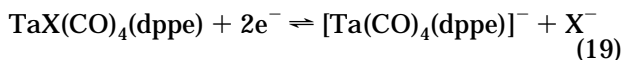
The compounds $\eta^1\text{-C}_3\text{H}_5\text{Ta}(\text{CO})_4(\text{dppe})$ and PhCH₂Ta(CO)₄(dppe) were apparently being observed in NMR tube reactions, where the compounds were formed and kept in the dark, but not in IR reactions, where the samples were exposed to fluorescent lighting. To check the possibility that light-sensitive organotantalum compounds were being prepared, as in eq 18, we reacted [Et₄N][Ta(CO)₄(dppe)] with benzyl bromide in THF. Under fluorescent lighting, only very weak carbonyl

bands were observed after 5 min and these were difficult to identify; the sample had largely decomposed. In contrast, a reaction run in the dark was completed within 5 min, and an IR spectrum of the reaction mixture exhibited bands corresponding to $\text{TaBr}(\text{CO})_4(\text{dppe})$ and a second compound. The latter, with carbonyl bands at 2000 (m), 1996 (m), and 1868 (vs) cm^{-1} , very similar to those of $\text{TaH}(\text{CO})_4(\text{dppe})$, is probably the benzyl complex, $\text{PhCH}_2\text{Ta}(\text{CO})_4(\text{dppe})$. No effort was made to isolate the benzyl compound in view of its apparent sensitivity to visible light. However, perhaps consistent with the low stabilities of the two presumed alkyltantalum compounds, it has been reported that the methyl analogue $\text{TaMe}(\text{CO})_2(\text{dmpe})_2$ contains an unusually long Ta–Me bond³³ and thus a presumption of low stability for σ -allyl and benzyl compounds seems warranted.

Reactions of $\text{TaH}(\text{CO})_4(\text{dppe})$ and $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_4(\text{dppe})]$ with benzyl bromide in toluene were very slow, very weak bands corresponding to $\text{TaBr}(\text{CO})_4(\text{dppe})$ being observed only after 15 min. Reaction of $\text{Ta}(\text{CO})_4(\text{dppe})$ with $(t\text{-BuC}_6\text{H}_4)_3\text{CBr}$ in toluene, monitored by IR spectroscopy, occurred instantly to form $\text{TaBr}(\text{CO})_4(\text{dppe})$.

The results of the reactions of $\text{Ta}(\text{CO})_4(\text{dppe})$ with organic halides are clearly distinguishable from the much slower reactions of $\text{TaH}(\text{CO})_4(\text{dppe})$ and, thus, do not somehow involve the hydride as an intermediate. However, the reaction products are as anticipated from a metal-centered radical and support our conclusions, based on physical properties, that $\text{Ta}(\text{CO})_4(\text{dppe})$ exists as such in solution. The relative rates of the homologous series of alkyl iodides and the relatively high rates of reaction of $\text{C}_3\text{H}_5\text{Br}$, PhCH_2Br , and $(t\text{-BuC}_6\text{H}_4)_3\text{CBr}$, although the data are qualitative, are exactly as expected for processes in which a metal-centered radical abstracts halogen atoms (eq 17). And while most of the reactions were too slow for alkyltantalum products to be observed, the light-sensitive products of the rapid reactions of $\text{Ta}(\text{CO})_4(\text{dppe})$ with $\text{C}_3\text{H}_5\text{Br}$ and PhCH_2Br are almost certainly as formulated.

Electrochemical Results. During the course of our investigation, a paper appeared detailing through voltammetry and IR spectroelectrochemistry the reduction of the Ta(I) complexes $\text{TaX}(\text{CO})_4(\text{dppe})$, X = Br, I.²¹ These results, by Blaine and co-workers, are relevant to the present work owing to the fact that the 18-electron anion $[\text{Ta}(\text{CO})_4(\text{dppe})]^-$ is formed upon reduction of the halide complexes (eq 19). Re-oxidation of



$[\text{Ta}(\text{CO})_4(\text{dppe})]^-$ in the presence of X^- re-forms the original halide complex in addition to some $\text{TaH}(\text{CO})_4(\text{dppe})$.²¹ In the context of our interest in the 17-electron radical $\text{Ta}(\text{CO})_4(\text{dppe})$, we were meanwhile pursuing studies of the oxidation of the 18-electron anion in order to probe the lifetime of the radical and establish a formal potential for the couple $[\text{Ta}(\text{CO})_4(\text{dppe})]^{0/-}$.

We have studied the oxidation of $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_4(\text{dppe})]$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{Bu}_4\text{N}][\text{PF}_6]$ by cyclic voltammetry, bulk coulometry, and IR spectroelectrochemistry. Be-

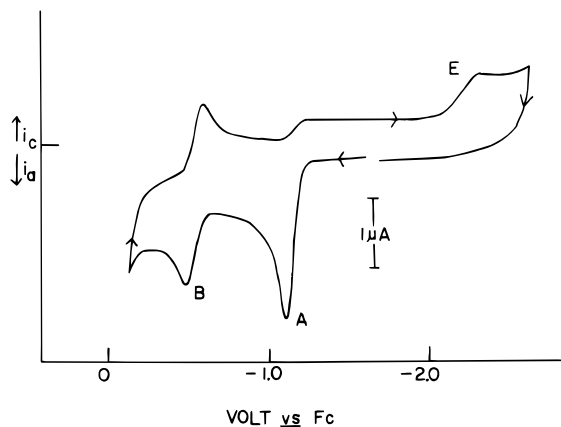


Figure 7. CV scan of 1 mM $[\text{Et}_4\text{N}][\text{Ta}(\text{CO})_4(\text{dppe})]$ in CH_2Cl_2 at Pt electrode, with $T = 245 \text{ K}$ and $\nu = 0.5 \text{ V/s}$. Arrows show progress of the scan.

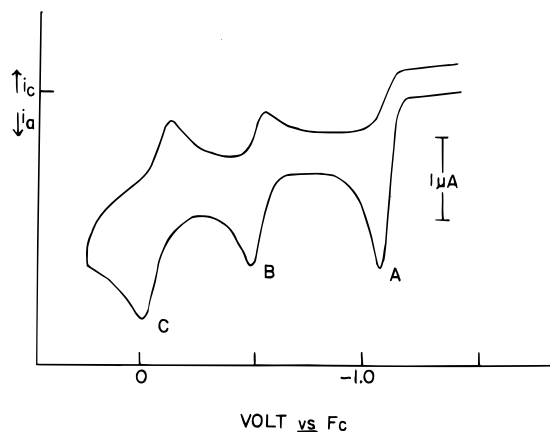


Figure 8. CV scan of 0.85 mM $[\text{Et}_4][\text{Ta}(\text{CO})_4(\text{dppe})]$ to more positive potentials than those of Figure 7. Conditions: solvent = CH_2Cl_2 , $T = 249 \text{ K}$, Pt electrode, $\nu = 1 \text{ V/s}$.

cause our results with the last of these are in basic agreement with the conclusions of Blaine *et al.*, indicating formation of $\text{TaH}(\text{CO})_4(\text{dppe})$ as well as other products during thin-layer electrolysis, the spectroelectrochemical results will not be presented. Rather, we concentrate on voltammetric data that give additional insight into the anodic mechanism of $[\text{Ta}(\text{CO})_4(\text{dppe})]^-$.

The anionic complex $[\text{Ta}(\text{CO})_4(\text{dppe})]^-$ was studied by cyclic voltammetry, and oxidation was found to be chemically irreversible in THF ($E_{\text{pa}} = -1.10 \text{ V}$), CH_2Cl_2 ($E_{\text{pa}} = -1.10 \text{ V}$), and *o*-difluorobenzene ($E_{\text{pa}} = -1.07 \text{ V}$) (potentials quoted for $\nu = 0.1 \text{ V/s}$). We show below that the anodic current function ($I_{\text{pa}}/\nu^{1/2}$, independent of ν) (wave A, Figure 7) corresponds to passage of ~ 1 electron. This feature is followed by a reversible oxidation (wave B, Figure 7) of about half the Faradaic intensity with $E_{1/2} = -0.48 \text{ V}$ in CH_2Cl_2 and -0.49 V in difluorobenzene. If the scan was continued to more positive potentials, another apparently reversible oxidation was observed ($E_{1/2} = -0.1 \text{ V}$, wave C, Figure 8). Yet another (quasi-reversible) anodic wave (E, not shown) appears at $E_{1/2} = +0.41 \text{ V}$ and is of about the same height as that of wave B. Scanning to highly negative potentials after first scanning through wave A gave a broad and irreversible cathodic feature (wave D, Figure 7). The processes responsible for product waves B–E were identified by matching their potentials

(33) Protasiewicz, J. D.; Bianconi, P. A.; Williams, I. D.; Liu, S.; Rao, C. P.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 4134.

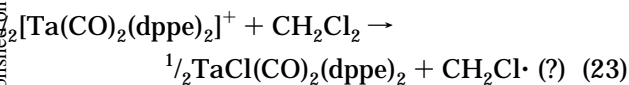
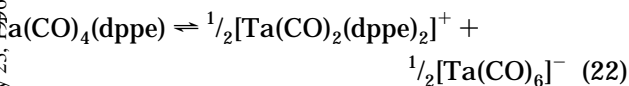
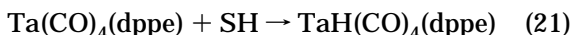
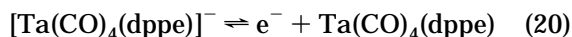
Table 5. Electrochemical Data of Tantalum Complexes with Potentials in V vs Ferrocene and Supporting Electrolyte 0.1 M [Bu₄N][PF₆]

complex	solvent	process	variable	potential	refs
[Ta(CO) ₆] ⁻	CH ₂ Cl ₂	oxdn	<i>E</i> _{pa}	~-0.5	this work
[Ta(CO) ₄ (dppe)] ⁻	CH ₂ Cl ₂	oxdn	<i>E</i> _{pa}	-1.10	this work
[Ta(CO) ₄ (dppe)] ⁻	THF	oxdn	<i>E</i> _{pa}	-1.16	21
TaH(CO) ₄ (dppe)	CH ₂ Cl ₂	0/+	<i>E</i> _{1/2}	-0.09	this work
TaBr(CO) ₄ (dppe)	CH ₂ Cl ₂	oxdn	<i>E</i> _{pa}	+0.41	21
TaI(CO) ₄ (dppe)	CH ₂ Cl ₂	oxdn	<i>E</i> _{pa}	+0.39	21
TaCl(CO) ₂ (dppe) ₂	CH ₂ Cl ₂	0/+	<i>E</i> _{1/2}	-0.44	this work
TaCl(CO) ₂ (dppe) ₂	CH ₂ Cl ₂	+/-2+	<i>E</i> _{1/2}	+0.42	this work
TaCl(CO) ₂ (dppe) ₂	DFB	0/+	<i>E</i> _{1/2}	-0.49	this work
TaCl(CO) ₂ (dppe) ₂	DFB	+/-2+	<i>E</i> _{1/2}	+0.32	this work

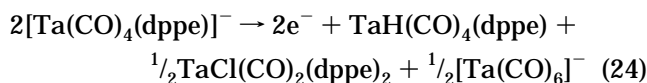
with those of independently prepared compounds suspected to be reaction products. Relevant potentials are collected in Table 5.

Figure 7 suggests that the oxidation of [Ta(CO)₄(dppe)]⁻ gives rise to a mixture of electroactive products with oxidations at *E*_{1/2} = -0.48 and -0.1 V (waves B and C, respectively). These potentials are matched by those of TaCl(CO)₂(dppe)₂ (*E*_{1/2} = -0.44 V) for wave B and the expected hydride product TaH(CO)₄(dppe) (*E*_{1/2} = -0.09 V)³⁴ for wave C. The presence of TaCl(CO)₂(dppe)₂ is confirmed by the anodic wave E (+0.42 V) measured for TaCl(CO)₂(dppe)₂^{+/-2+}, +0.41 V in Figure 7, which corresponds to the second one-electron oxidation of the chloro complex.

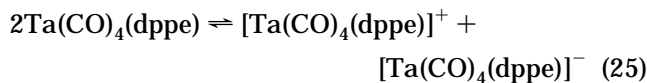
The mechanism in eqs 20–23 accounts for the observed product waves. In this scenario, once the 17-electron radical is formed (eq 20) it is subject to two



major pathways for subsequent reactions, namely hydrogen atom abstraction from the solvent (SH) or the electrolyte cation [eq 21, giving TaH(CO)₄(dppe), wave C] and ionic disproportionation with ligand exchange (eq 22), producing the 16-electron species [Ta(CO)₂(dppe)₂]⁺, which then abstracts halide from the solvent (eq 23) or, possibly, chloride-containing, adventitious impurities. The chloride abstraction reaction gives TaCl(CO)₂(dppe)₂, the oxidation of which is responsible for waves B and E. A net transfer of one electron/equiv of [Ta(CO)₄(dppe)]⁻ is predicted by the overall reaction (eq 24). No direct voltammetric evidence for [Ta(CO)₆]⁻ was obtained, not surprising owing to its poor electrochemical behavior (*vide infra*). The net overall reaction for tantalum-containing species is then



We must also consider the possibility that Ta(CO)₄(dppe) reacts by simple ionic diproportionation (eq 25)



giving the 16-electron species [Ta(CO)₄(dppe)]⁺, which could form the hydride TaH(CO)₄(dppe) and, perhaps, TaCl(CO)₄(dppe) through hydride and halide abstraction, respectively, from the solvent. We cannot rule out TaCl(CO)₄(dppe) as a possible product since it is expected²¹ to have an oxidation wave in the vicinity of +0.4 V (near wave E); ambiguity arises because TaCl(CO)₂(dppe)₂ has a wave at the same potential arising from its oxidation to a dication.

The strongest evidence against eq 25 being an important part of the mechanism comes from the observed electron stoichiometry. Note that the simple disproportionation of eq 25 returns 1 equiv of the starting anion to the reaction sequence, so that a *net two electrons/equiv* of [Ta(CO)₄(dppe)]⁻ is required when eqs 20 and 25 are combined, in contrast to the *one-electron* stoichiometry predicted from eq 24.

The actual electron stoichiometry was measured by two methods, (a) bulk coulometry and (b) comparison of voltammetric peak heights of [Ta(CO)₄(dppe)]⁻ with a suitable standard. Exhaustive electrolysis was performed a number of times at various temperatures, and a net stoichiometry of 0.7–0.9 electrons/mol of [Ta(CO)₄(dppe)]⁻ was obtained on each occasion. We take this to be consistent with an overall *n*_{app} = 1 electron process (eq 24).

For approach (b), it is important to employ a standard with a diffusion coefficient similar to that of [Ta(CO)₄(dppe)]⁻. With this in mind we used [CpMo(CO)₃]⁻ (*E*_{pa} ~ -0.55 V vs Fc) owing to its similar size and identical charge. This anion is reported to give a one-electron oxidation in CH₂Cl₂.^{35,36} The current functions of [CpMo(CO)₃]⁻ and [Ta(CO)₄(dppe)]⁻ in CH₂Cl₂ were virtually identical at concentrations of either 0.3 or 0.7 mM, leading us to again conclude that the primary oxidation wave of [Ta(CO)₄(dppe)]⁻ (wave A) is a *one-electron* process.

The species giving rise to the small and broad reduction wave D in Figure 7 is uncertain. Both TaH(CO)₄(dppe) and TaX(CO)₄(dppe) have irreversible waves in this region, and other possibilities exist as well.

One fact deserving mention is that wave B comes at virtually the same potential in both CH₂Cl₂ and *o*-difluorobenzene. At first sight this appears to argue against assignment of wave B as TaCl(CO)₂(dppe)₂ in the former [and TaF(CO)₂(dppe)₂ in the latter]. The waves for the two possible halide products may, however, be coincidental, and it is known that the identity of X has very little effect on the potentials of compounds of the types TaX(CO)₄(dppe) or TaX(CO)₂(dppe)₂.^{21,37}

(35) Kadish, K.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

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(37) Bond, A. M.; Bixler, J. W.; Mocellin, E.; Datta, S.; James, E. J.; Wreford, S. S. *Inorg. Chem.* **1980**, *19*, 1760.

(34) In ref 21, the potential of the oxidation of TaH(CO)₄(dppe) is given as -0.48 V vs Fc. For this system we obtain a value of -0.09 V vs Fc (±0.01 V) in several experiments in CH₂Cl₂ and -0.03 V in *o*-difluorobenzene.

The possibility also exists that wave B arises from TaF(CO)₂(dppe)₂ in both solvents, with the supporting electrolyte anion, [PF₆]⁻, acting as the source of fluoride ion in both cases.

Voltammetry experiments conducted at high sweep rates (up to $v = 50$ V/s at 273 K in CH₂Cl₂) failed to reveal any reversibility for the oxidation of [Ta(CO)₄(dppe)]⁻. This observation is in contrast to the much greater stability of Ta(CO)₄(dppe) in nonionic media, reflecting the additional reaction pathways available to the radical in ionic solutions. Although the chemical irreversibility of the couple [Ta(CO)₄(dppe)]^{0/-} precludes a precise measure of its formal potential, the

$E_{1/2}$ value must lie close to -1.2 V vs Fc. Reasonable limits for this quantity are -1.2 V \pm 0.1 V.

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