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Electrochemical and Chemical Oxidation of Seven-Coordinate Group 5 Complexes

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Studies on a range of seven-coordinate tantalum(II) and niobium(II) complexes and other tantalum(III) and tantalum(IV) complexes illustrate a very general observation that 18-electron transition-metal organometallic complexes containing bidentate phosphorus ligands, regardless of geometry, oxidation state, or element, can usually be reversibly oxidized via electrochemical techniques to produce relatively stable compounds having 17-electron configurations. The ability of bidentate phosphorus ligands to promote the oxidation of organometallic species to 17-electron systems in, formally, unusual oxidation states is considered in terms of an internal disproportionation reaction delocalizing electron density onto the phosphorus orbitals.

An extraordinarily wide range of organometallic complexes containing monodentate and bidentate phosphorus ligands have been prepared and characterized.¹ Many of these complexes have unusual and interesting properties, as revealed by exhaustive examination by almost every conceivable method of physical measurement.¹ The use of the bidentate ligands 1,2-bis(diphenylphosphino)ethane (DPE), bis(diphenylphosphino)methane (DPM), and 1,2-bis(dimethylphosphino)ethane (DMPE) is particularly ubiquitous. Transition-metal complexes of these ligands, having a variety of geometries, stereochemistries, and coordination numbers, are known. For example, the complexes Ni(DPE)₂,² Fe(CO)₃(DPE),³ Mo(CO)₂(DPE)₂,⁴ Ta(CO)₂(DMPE)₂Cl,⁵ and Re₂Cl₄(DPE)⁶ represent a range of well-documented species exhibiting substantially different structural features and oxidation states.

Electrochemical and chemical redox studies have been made on a number of complexes containing bidentate phosphorus ligands.^{3,6-10} A generally observed characteristic in most of these studies, regardless of the transition metal present or its geometry, is the observation of electrode processes leading to the production of remarkably stable products in unusual formal oxidation states. Much of this work has involved oxidation of mixed carbonyl phosphorus complexes, and from the collection of data now available, some generalizations and rationalizations may be made.

For example, the available literature indicates that oxidation of unsubstituted, 18-electron, binary transition-metal carbonyl complexes is extremely difficult. Oxidation occurs at very positive potentials, generating observable, in rare instances, but very reactive (unstable) 17-electron cations.¹¹⁻¹⁵ Substitution of carbonyl groups by phosphorus (and other) ligands^{14,15} shifts the oxidation potentials to very much less positive potentials and stabilizes the product, making possible the generation of 17-electron cations with mild chemical oxidants. Substitution by tertiary phosphines, therefore, facilitates the synthesis of 17-electron cations, some of which are remarkably stable. For example, molybdenum hexacarbonyl is extremely difficult to oxidize; the cation Mo(CO)₆⁺ is not observable on the electrochemical time scale in a range of media.^{11,12} However, *cis*-Mo(CO)₂(DPE)₂ can be oxidized with iodine to produce the extremely stable *trans*-[Mo^I(CO)₂(DPE)₂]⁺ (formally molybdenum I), which can then be examined by the entire spectrum of physicochemical methods.¹⁶ Similarly, the (formally) iron(I) species, [Fe(CO)₃(DPE)]⁺,³ is substantially more stable than [Fe(CO)₅]⁺¹¹⁻¹³ or even than [Fe(CO)₃(PPh₃)₂]⁺.³

One important geometric configuration, omitted from previous investigations and required to further test the applicability of the above generalization, is the oxidation of

species with a coordination number of seven. Recently, Wreford et al.^{5,17-19} have prepared and investigated a range of complexes of the type M(CO)₂(P-P)₂X [M = Ta, Nb; P-P = DMPE, 1-(dimethylphosphino)-2-(diethylphosphino)ethane (DMDEPE), and related unsymmetric bidentate phosphines; X = Cl, Br, I, H, CH₃]. Unlike most of the species previously investigated, these 18-electron complexes are easily oxidized by air; air oxidation does not, however, generate an observable 17-electron, Ta(II) or Nb(II) cation. Prior to this work, no evidence for seven-coordinate, 17-electron tantalum species had been presented. Related 17-electron niobium(IV), tantalum(IV), and zirconium(III) cyclopentadienyl complexes have been prepared. Thus, photolytically generated *tert*-butoxy radicals abstract hydrogen atoms from (η-C₅H₅)₂NbH₃, affording short-lived (η-C₅H₅)₂NbH₂ (t_{1/2} at -70 °C ~ 10 min).^{20,21} Methyl-substituted analogues (η-C₅H₅)₂Nb(CH₃)₂ and (η-C₅H₅)₂Ta(CH₃)₂ are stable and have been isolated,²² as are derivatives with bulky alkyl groups.²³ Isoelectronic Zr(III) complexes have been prepared and observed in situ.²⁴ These data, taken with the apparent increase in stability imparted to 17-electron species by phosphino substitution (*vide supra*), suggest that electrochemical oxidation of M(CO)₂(P-P)₂X (M = Ta, Nb) should result in the formation of moderately stable M(II), 17-electron cations. Further, since the formation of high-coordination number complexes is a common

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feature of the early transition metals, the chemistry and stability of oxidatively formed, seven-coordinate cations might have broad implications.

The purpose of the present communication is to provide direct evidence for 17-electron tantalum(II) and related cations and to present some observations concerning their stability and decomposition pathways. An isoelectronic niobium(I) complex, a non-carbonyl-containing Ta(I) complex, and bis(cyclopentadienyl)tantalum(III) complexes containing a bidentate phosphorus ligand are also included in this report to further indicate the general role of such ligands in stabilizing cationic species. Both electrochemical and chemical methods of oxidation have been examined in these studies.

Experimental Section

Chemicals and Solvents. All compounds used for electrochemical studies were prepared by literature methods^{5,17-19} except for $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{BF}_4$ and $[(\eta\text{-C}_5\text{H}_5\text{Me})_2\text{Ta}(\text{DMPE})](\text{BF}_4)_2$ (see later). After preparation the compounds were stored in evacuated glass ampules. The subsequent manipulations and preparations required for electrochemical investigation of species decomposing in air in less than 1 min were undertaken in a drybox. All compounds were added as rapidly as possible as accurately weighed solids to known volumes of thoroughly degassed (argon or nitrogen) solutions of solvent/electrolyte at a temperature of $22 \pm 1^\circ\text{C}$, unless otherwise stated, and electrochemical experiments were commenced immediately after the solid had dissolved. Concentrations of the complexes in the range 10^{-3} to 5×10^{-3} M were prepared in the above manner in acetone (0.1 M Et_4NClO_4), acetonitrile (0.1 M Et_4NClO_4), or dichloromethane (0.07 M Et_4NClO_4).

The compounds $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{TaBr}_2$ ²² and DMPE ²⁵ were prepared by literature procedures. Solvents for synthetic work were distilled from sodium benzophenone ketyl, excepting CH_2Cl_2 and CH_3CN which were purified by distillation from P_2O_5 and CaH_2 , respectively. Manipulations were performed under an atmosphere of prepurified nitrogen or argon. ESR spectra (9.5 GHz) were obtained with a Varian E-109 spectrometer. Elemental analyses were performed by Alfred Bernhardt Microanalytische Laboratorium, West Germany.

Electrochemistry. Polarograms and cyclic voltammograms were recorded on either a PAR electrochemistry system, Model 170, or a PAR polarographic analyzer, Model 174A. For studies in dichloromethane, 0.07 M tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte. In acetone and acetonitrile, 0.1 M TEAP was used as the supporting electrolyte. Ag/AgCl (saturated LiCl in acetone), separated from the test solution via a salt bridge containing the electrolyte/supporting electrolyte, was used as a reference electrode. A three-electrode system, employing positive feed-back circuitry, was used on all occasions with platinum wire as the auxiliary electrode. The working electrode was either a platinum wire or a dropping mercury electrode. For the cyclic voltammograms at the dropping mercury electrode, the potential scan was commenced 1 s after the start of the drop. This and other timing sequences for this technique were controlled by a PAR linear sweep accessory module 174/51. Further details of operating conditions are given at appropriate places in the text and figures. Solutions were thoroughly degassed with argon or nitrogen prior to recording a polarogram or voltammogram (see above).

Controlled-potential electrolysis experiments were performed at mercury pool and platinum gauze electrodes using a PAR Model 173 potentiostat in conjunction with a Model 9600 coulometry cell system and Model 179 digital coulometer. A three-electrode system was used with platinum gauze as the auxiliary electrode separated from the test solution by a porous Vycor sinter. The supporting electrolyte solutions and the reference electrodes were the same as for the polarography and voltammetry. The test solution was stirred during the course of the experiment and a stream of argon was passed over the solution at all times. The platinum working electrode was thoroughly cleaned in 6 M nitric acid and carefully washed with solvent before each use.

$[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{BF}_4$. The complex $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{TaBr}_2$ (2.54 g, 5.0 mmol) was suspended in 50 mL of THF and treated with 7.1 mL of a 0.7 M solution of sodium naphthalene in THF, followed

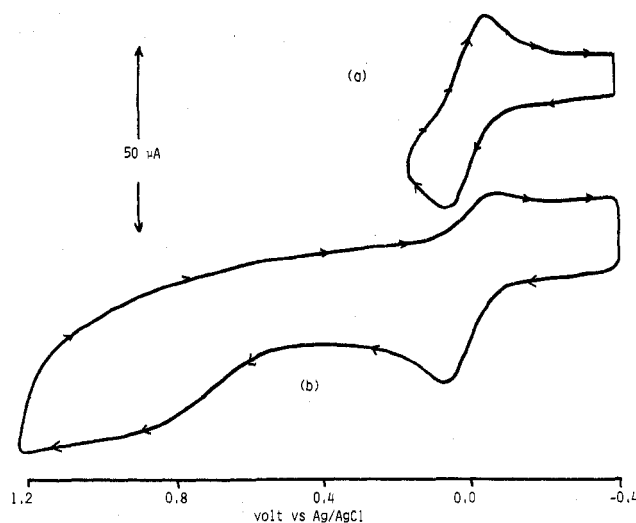


Figure 1. Cyclic voltammogram for oxidation of $\text{Ta}(\text{CO})_2(\text{DMDEPE})_2\text{Cl}$ at a platinum electrode in acetone at 22°C : scan rate = 500 mV/s; concentration approximately 2×10^{-3} M.

by 0.830 mL of DMPE. The resulting purple solution was refluxed overnight, affording a red suspension. After evaporation of the solvent, the residue was washed with several portions of benzene and then extracted with 2×100 mL of CH_2Cl_2 . The pooled extracts were filtered and evaporated to dryness, affording 1.97 g of a red solid. The product, $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{Br}$, was then converted to the more easily purified tetrafluoroborate salt. Thus, 0.8017 g (1.41 mmol) of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{Br}$ was dissolved in a minimum of deoxygenated water and treated with a tenfold excess of an aqueous solution of NaBF_4 . The resulting orange precipitate was collected by filtration, washed with water, and dried in vacuo, affording 0.671 g (1.16 mmol, 83%). An analytical sample was recrystallized by concentration of a $\text{CH}_2\text{Cl}_2/\text{THF}$ solution: $^1\text{H NMR}$ (CD_2Cl_2) 5.20 (m, 4 H), 5.61 (m, 4 H), 7.96 (s, 6 H), 8.45 (overlapping multiplets, 16 H, DMPE protons).

Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{BF}_4\text{P}_2\text{Ta}$: C, 37.52; H, 5.25. Found: C, 37.90; H, 5.21.

$[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{BF}_4$. Dropwise addition of a solution of 210 mg (0.637 mmol) of $[\text{Ph}_3\text{C}][\text{BF}_4]$ in 5 mL of CH_2Cl_2 to 368.2 mg (0.639 mmol) of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{Br}$ dissolved in 2 mL of CH_2Cl_2 resulted in the formation of a yellow precipitate and a red solution. The precipitate was collected by filtration, washed with additional CH_2Cl_2 , and dried in vacuo, affording 264.5 mg (0.399 mmol, 62%) of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})]\text{BF}_4$. Although the complex is soluble in acetonitrile or Me_2SO , it decomposes in solution too rapidly to allow purification by recrystallization.

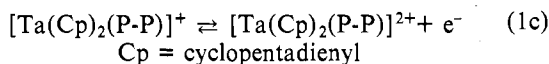
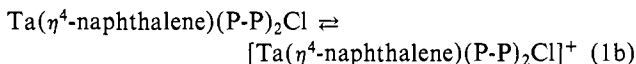
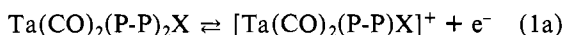
ESR (CH_3CN , 283 K) $g = 1.9947$, $a_{181\text{Ta}} = 42$, $a_{31\text{P}} = 29$ G. Magnetic moment²⁶ (CH_3CN solution) $\mu_{\text{eff}}(272.8 \text{ K}) = 1.68 \mu_{\text{B}}$. Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{B}_2\text{F}_8\text{P}_2\text{Ta}$: C, 32.61; H, 4.56. Found: C, 31.89; H, 4.50.

Results and Discussions

Electrochemical Oxidation at Platinum Electrodes. All of the complexes examined, regardless of solvent, metal, presence or absence of carbonyl groups, number of bidentate phosphorus ligands, or oxidation state, exhibit two main oxidation waves at platinum electrodes under conditions of cyclic voltammetry. Figure 1a shows a cyclic voltammogram of the first oxidation process for the complex $\text{Ta}(\text{CO})_2(\text{DMDEPE})_2\text{Cl}$ in acetone. In each case, when the potential scan direction is switched prior to reaching the potential region where the second process is observed, a chemically reversible one-electron oxidation step is established, as evidenced by a unity ratio of the oxidation to the reduction peak height. The separation of oxidation and

(26) Determined by the Evans method (Evans, D. F. *J. Chem. Soc.* 1959, 2003.) using Pascal's constants for estimating the diamagnetic correction (Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: New York, 1968; p 4.).

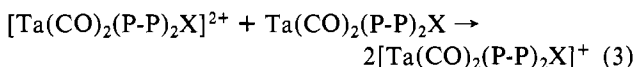
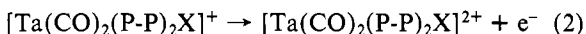
reduction peaks for the first oxidation process under conditions of cyclic voltammetry is rather variable from solvent to solvent and from complex to complex. Nevertheless, such data are consistent in all cases with a quasi-reversible electron-transfer process. The first step can, therefore, be assigned to the electrode processes



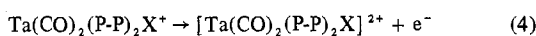
Indeed, the generation of a 17-electron cation, stable on the electrochemical time scale, is observed for all the complexes examined.

The nature of the second wave varies substantially, depending on conditions, solvent, and complex. However, for all the seven-coordinate species it is chemically completely irreversible over all scan rates from 50 mV/s to 5 V/s and temperatures from 22 to -75 °C. Furthermore, scanning to more positive potential than the second process substantially influences the nature of the first, reversible, one-electron electrode process, as seen in Figure 1b.

All of the data on the chemically irreversible second electrode processes are consistent with the product of the second process interacting with the first redox couple. Equivalent experiments to those of Vleck et al.²⁷ on the reduction of $\text{Fe}_3(\text{CO})_{12}$ provide analogous data to that obtained by these workers. Therefore, results can be interpreted similarly. That is, one of the important mechanisms associated with the decay of the product of the second process may be as indicated in eq 2 and 3. Analogous equations can be written to explain



a significant fraction of the electrochemistry of the other seven-coordinate species. Equation 3 is not proven; i.e., other intermediates, generated during the electrochemical experiment, could react with $\text{Ta}(\text{CO})_2(\text{P-P})_2\text{X}$ and satisfy the data. The important feature, established unambiguously for all the seven-coordinate species containing bidentate phosphorus ligands, is that the 16-electron, dipositive cation is extremely reactive and shows no inherent stability on the electrochemical time scale. A completely general description of the second electrode process encompassing all seven-coordinate species would, therefore, be as follows:



↓
products

The second electrode process for $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{DMPE})]^+$ is chemically reversible, as shown in Figure 2. The enhanced stability of the two-electron oxidation product, $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{DMPE})]^{3+}$, is anticipated, as the isoelectronic, 16-electron, group 4 derivatives $(\eta\text{-C}_5\text{H}_5)_2\text{MR}_2$ (R = halogen, methyl, aryl groups; M = Ti, Zr, Hf) are well-known,²⁸ bis-(cyclopentadienyl)tantalum(V) complexes have been isolated,

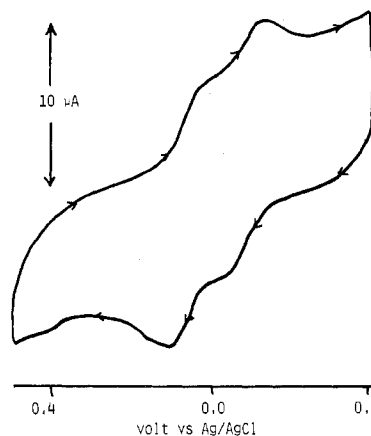


Figure 2. Cyclic voltammogram of $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{DMPE})][\text{PF}_6]$ in acetone at 22 °C: scan rate = 500 mV/s; concentration approximately 5×10^{-4} M.

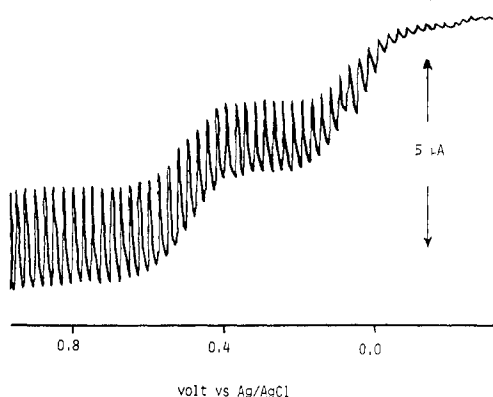


Figure 3. Dc polarogram of $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Cl}$ in dichloromethane at 22 °C: drop time = 0.5 s; concentration of complex approximately 3×10^{-3} M.

e.g., $(\eta\text{-C}_5\text{H}_5)_2\text{TaH}_3$ ²⁹ and $(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_3)_3$.³⁰

Controlled-potential electrolysis of all the seven-coordinate complexes at a platinum electrode in each of the three solvents at a potential corresponding to the first oxidation step proved difficult because of the instability of the starting material. Coulometric values obtained from such controlled-potential electrolysis experiments were, therefore, not highly accurate but n values of 0.5 ± 0.2 were observed. However, no evidence for a seven-coordinate 17-electron cation, stable at ambient temperatures on the synthetic time scale, could be found, despite the electrochemical data indicating that such species exist with half-lives of at least 0.1 s. The apparent n value from coulometry of 0.5 ± 0.2 suggests that a decomposition product, derived from the cation, reacts with the starting material. The information from controlled-potential electrolysis experiments at platinum, coupled with that from other electrochemical data, demonstrates that a very pronounced order of chemical stability exists in solution. That is, in terms of electronic configuration the order of stability is clearly 18 electron \gg 17 electron \gg 16 electron.

Electrochemical Oxidation at Mercury Electrodes. Electrode processes at mercury were frequently more complex than at platinum because of adsorption and maxima (under polarographic conditions). However, considerable parallels were established in that the first process was found to be chemically reversible by cyclic voltammetry. The second process frequently occurred at very different potentials to those at Pt.

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Table I. Voltammetric and Polarographic Data for Tantalum and Niobium Complexes^a

compound	solvent ^b	cyclic voltammetry ^c			polarography ^d $E_{1/2}$ (V) vs. Ag AgCl	comments
		$(E_p)_{Ox}$ (V) vs. Ag AgCl	$(E_p)_{Red}$ (V) vs. Ag AgCl	elec- trode		
Ta(CO) ₂ (DMPE) ₂ Cl	acetone	+0.12	-0.05	Pt	+0.02	
	acetone	+0.55	none	Pt	+0.32	
	dichloromethane	+0.28	-0.05	Pt	+0.08	
Ta(CO) ₂ (DMPE) ₂ Br	dichloromethane	+0.9	none	Pt	+0.50	
	acetone	+0.09	+0.01	Pt	+0.04	
Ta(CO) ₂ (DMPE) ₂ I	acetone	+0.8	none	Pt	+0.60	
	acetone	+0.16	+0.04	Pt	+0.10	
	acetone	+0.8	none	Pt		polarogram in acetone appears to be two very closely spaced one-electron oxidation processes
	dichloromethane	+0.48	+0.00	Pt	+0.24	
Ta(CO) ₂ (DMPE) ₂ CH ₃	dichloromethane	+1.0	none	Pt	+0.45	
	acetone	-0.10	-0.26	Pt	-0.28, -0.18	polarographic waves with $E_{1/2}$ -0.28 and -0.18 in combination are equivalent to a one-electron oxidation step
Ta(CO) ₂ (DMPE) ₂ H	acetone	+0.60	none	Pt	+0.07	
	acetone	-0.32	-0.46	Pt	not measd	very unstable compound which decomposed during recording of polarograms; small reversible wave around 0 V observed at Pt (origin uncertain)
Ta(CO) ₂ (DMDEPE) ₂ Cl ^e	acetone	+0.44	none	Pt	because of dec	
	acetone	-0.05	+0.08	Pt	-0.05	additional waves seen on cyclic at Hg when switching potential more positive than second oxidation process
	acetone	+0.66	none	Pt	+0.38	
	acetone	0.00	-0.08	Hg		
	dichloromethane	+0.32	-0.12	Pt	-0.05	
	dichloromethane	+0.8	none	Pt	+0.37	
	dichloromethane	+0.12	-0.02	Hg		
	dichloromethane	+0.67	none	Hg		
	acetonitrile	+0.04	-0.08	Pt	-0.04	
	acetonitrile	+0.9	none	Pt	+0.40	
	acetonitrile	0.00	-0.09	Hg		
Nb(CO) ₂ (DMPE) ₂ Cl	acetonitrile	+0.60	none	Hg		
	acetone	+0.20	-0.02	Pt	+0.10	
	acetone	+0.8	none	Pt	+0.45	
	dichloromethane	+0.35	-0.02	Pt	+0.12	
Ta(η^4 -naphthalene)(DMPE) ₂ Cl	dichloromethane	+1.1	none	Pt	+0.48	
	acetone	-0.46	-0.54	Pt	-0.51	other processes complicated by adsorption and maxima observed at mercury electrodes
[(η -C ₅ H ₅) ₂ Ta(DMPE)]PF ₆	acetone	-0.13	none	Pt		
	acetone	-0.05	-0.12	Pt	-0.12	
	acetone	+0.15	+0.05	Pt	+0.08	
[(η -C ₅ H ₄ Me) ₂ Ta(DMPE)]BF ₄	acetone	-0.05	-0.15	Hg		
	acetone	+0.15	+0.05	Hg		
	acetone	+0.14	+0.04	Pt	0.080	
[(η -C ₅ H ₄ Me) ₂ Ta(DMPE)][BF ₄] ₂	acetone	+1.28	none	Pt		
	acetone	+0.04 ^f	+0.14 ^f	Pt	0.080 ^f	reduction wave with $E_{1/2}$ = 0.080 coincides exactly with oxidation wave for [(η -C ₅ H ₄ Me) ₂ Ta(DMPE)]BF ₄
	acetone	+1.28	none	Pt		

^a DMPE = 1,2-bis(dimethylphosphino)ethene. DMDEPE = 1-dimethylphosphino-2-diethylphosphinoethane. Concentration of complex = $1-5 \times 10^{-3}$ M. ^b Supporting electrolyte = 0.1 M TEAP in acetone and acetonitrile and 0.07 M TEAP in dichloromethane. Temperature = 22 ± 1 °C. ^c Scan rate = 500 mV/s. ^d Drop time = 0.5 s. ^e This compound exists as two different isomers which are polarographically undifferentiated. ^f Reduction process, all other electrode processes are oxidation ones.

Figure 3 shows a dc polarogram for Ta(CO)₂(DMPE)₂Cl in dichloromethane; two one-electron oxidation steps of equal height are clearly seen in this example. For the [(η -C₅H₅)₂Ta(DMPE)]⁺ cation both oxidation processes were chemically reversible, as found with a platinum electrode. Substantial interaction with mercury, including the possibility of mercury complex formation, is indicated by the electrochemical studies of some of the compounds at mercury. This complication would need to be considered in providing a full description of the electrochemistry at mercury, but, since such information is outside the scope of the present investigation, the mercury interaction and electrochemical studies at the mercury electrode were only briefly examined under a limited set of conditions, as indicated in Table I.

Electrochemical Reduction of [(η -C₅H₄Me)₂Ta(DMPE)][BF₄]₂. Figure 4 shows dc polarograms for reduction of [(η -C₅H₄Me)₂Ta(DMPE)][BF₄]₂ and oxidation of [(η -C₅H₄Me)₂Ta(DMPE)][BF₄]. These two complexes at both platinum and mercury electrodes give rise to identical behavior except of course that the formally Ta(IV) complex gives a reversible one-electron reduction at the same potential where a reversible one-electron oxidation is seen for the Ta(III) complex. These data of course unambiguously confirm the existence of the closely related pair of complexes differing only in electronic configuration.

Chemical Oxidation. According to the electrochemical data, oxidation of the various species should be possible with mild oxidants such as silver(I) or triphenylmethyl cation. Oxidation

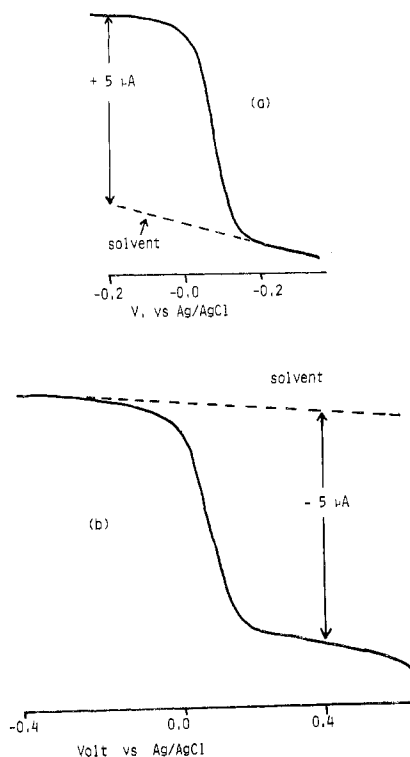


Figure 4. Dc polarograms for (a) reduction of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]_2$ and (b) oxidation of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]$ in acetone at 22 °C; drop time = 0.5 s; concentration of complexes = 2×10^{-3} M.

Table II. Comparison of Infrared and Electrochemical Data for $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{X}$ Complexes

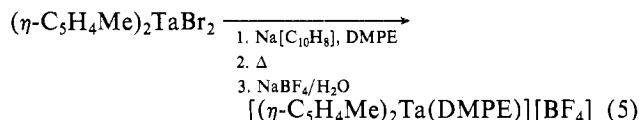
complex	$\text{IR},^a \text{ cm}^{-1}$ carbonyl bands		$E^\circ{}^b$
	ν_{sym}	ν_{antisym}	
$\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Cl}$	1833 vs	1765 s	+0.02
$\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Br}$	1832 vs	1765 s	+0.04
$\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{I}$	1838 vs	1769 s	+0.08
$\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{CH}_3$	1823 vs	1760 s	-0.20
$\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{H}^c$		1753 vs	-0.38

^a Tetrahydrofuran; error limit is $\pm 5 \text{ cm}^{-1}$. ^b $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{X} \rightleftharpoons [\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{X}]^+ + e^-$ acetone (0.1 M TEAP). Volt vs. Ag^+/AgCl . Calculated from cyclic voltammetry and polarographic data. Error limit is ± 0.02 V. ^c *trans*-Dicarbonyl structure.

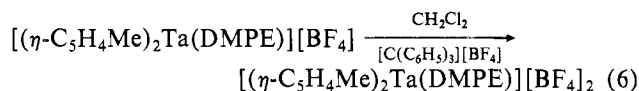
of the seven-coordinate complexes with silver perchlorate rapidly produced metallic silver, but no 17-electron cation could be observed as the end product, as evidenced by monitoring of the electrochemical response and by the absence of the ESR signal expected for such a species. Similarly, ESR spectroscopic monitoring of the addition of $[\text{C}(\text{C}_6\text{H}_5)_3][\text{BF}_4]$ to CH_2Cl_2 solutions of $\text{TaCl}(\text{CO})_2(\text{DMPE})_2$ or $\text{Ta}(\text{CH}_3)(\eta^4\text{-naphthalene})(\text{DMPE})_2$ established the formation of the trityl radical. However, no other ESR signals were observed, even when the additions were performed at -80 °C. Stable $\text{Ta}^{\text{II}}(\text{DMPE})_2$ complexes, e.g., $\text{TaCl}_2(\text{DMPE})_2$ have easily recognizable ESR spectra, owing to the large hyperfine interaction with ^{181}Ta ($I = 7/2$). Apparently, the seven-coordinate, 17-electron cations are too short lived to detect by static mixing experiments. For the carbonyl complexes, infrared evidence demonstrated that the final products were non-carbonyl-containing species. Similar observations were made when using mercuric(II) perchlorate as an oxidant. All of the data obtained from chemical oxidations of these complexes are consistent with the controlled-potential electrolysis experiments. That is, whilst the seven-coordinate, 17-electron cations can be observed on the time scale of cyclic voltam-

metry, they are not particularly stable and would be very difficult to isolate.

However, the cyclopentadienyl-substituted, 17-electron derivatives are substantially more stable. Thus, $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]$, prepared by sodium naphthalene reduction of $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{TaBr}_2$ in the presence of DMPE (eq 5), is oxidized by $[\text{C}(\text{C}_6\text{H}_5)_3][\text{BF}_4]$, affording the 17-electron,



$\text{Ta}(\text{IV})$ complex $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]_2$, as in eq 6. The yellow product is stable indefinitely as a solid; ace-



tonitrile solutions rapidly decompose to red, unidentified products unless cooled. The paramagnetic dication has a magnetic moment of $1.78 \mu_B$, consistent with a magnetically dilute, $S = 1/2$ system. The ESR spectrum shows the eight overlapping triplets expected for a $^{181}\text{Ta}^{31}\text{P}_2$ containing fragment.

The chemical oxidation of the unsubstituted derivative, $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{DMPE})][\text{BF}_4]$, was not investigated because of its lower solubility.

Correlation of Ease of Oxidation with Infrared Spectra of the Carbonyl Complexes. Table II shows a comparison of calculated E° values, obtained by using the theory of Shain and Nicholson,³¹ and IR data for the carbonyl complexes $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{X}$. The considerably more negative oxidation potentials observed when $\text{X} = \text{CH}_3$ correlates with the lower wavenumber of the stronger, symmetric carbonyl stretch. Indeed, as can be seen from these data, the correlation is extremely good and the substituent effects observed by varying the X group are paralleled in the two measurements, as has been observed elsewhere for carbonyl containing species.^{2,32-34}

Conclusions

For seven-coordinate tantalum(I) complexes containing bidentate phosphorus ligands, the data obtained in the present work demonstrate that, regardless of the geometry or the presence or absence of carbonyl groups, oxidation to 17-electron and 16-electron configurations can be achieved and that the electrode processes have remarkable similarities. For example, in the $\text{Ta}(\text{P-P})_2(\text{CO})_2\text{X}$ series when $\text{X} = \text{H}$, the carbonyl groups are *trans*;³⁴ when $\text{X} = \text{Cl}$, Br , I , or CH_3 , they are *cis*. Yet, in each case, a cation, $[\text{Ta}(\text{P-P})_2(\text{CO})_2\text{X}]^+$, is very readily produced and is moderately stable. At more positive oxidizing potentials, a very reactive 16-electron species, $[\text{Ta}(\text{P-P})_2(\text{CO})_2\text{X}]^{2+}$, can be formed in each case. Similarly, if all carbonyl groups are replaced by coordinated η^4 -naphthalene, the same oxidation behavior is observed. The isoelectronic niobium species $\text{Nb}(\text{CO})_2(\text{DMPE})_2\text{Cl}$ exhibits similar behavior, as do the isoelectronic, six-coordinate group 6 complexes, $\text{M}(\text{CO})_2(\text{P-P})_2$ ($\text{M} = \text{Cr}$, Mo , W).^{8,35,36} Electrochemical or chemical oxidation of the group 6 derivatives affords somewhat more stable 17-electron and reactive 16-electron cations. In contrast to the seven-coordinate Ta com-

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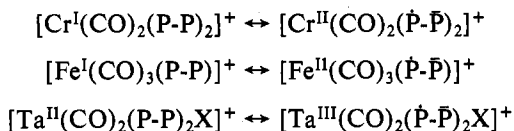
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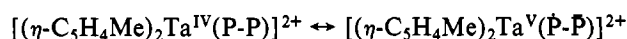
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plexes in this work, the group 6 17-electron cations, $[M(\text{CO})_2(\text{P-P})_2]^+$, are sufficiently stable that ESR data can be obtained. A substantial ^{31}P hyperfine interaction is observed in all cases. For example, $[\text{Cr}(\text{CO})_2(\text{P-P})_2]^+$ complexes give simple five-line spectra. Similarly, $[\text{Fe}(\text{CO})_3(\text{P-P})]^+$ species exhibit three-line spectra because of coupling with two equivalent phosphorus atoms.³

The data above suggest that bidentate phosphorus ligands have a remarkable ability to stabilize 17-electron systems in formally, unusual oxidation states. It is likely that this property arises from substantial delocalization of the unpaired electron onto the phosphorus atoms. That is, a stabilized species can be formed by transfer of an electron from the metal d levels to the phosphorus orbitals, leaving the metal in a common, stable oxidation state. For example



where $(\dot{\text{P}}-\dot{\text{P}})$ is a delocalized electronic configuration. These resonance structures are equivalent to an internal disproportionation; 17-electron systems commonly disproportionate in the usual sense to produce more stable configurations.³⁷⁻³⁹ The ^{181}Ta and ^{31}P hyperfine interactions observed in the ESR spectrum of $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]$ are consistent with this hypothesis; i.e., the Ta(V) resonance form makes an important contribution. Thus, $a_{181\text{Ta}}$ (42 G) is



substantially smaller than for $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{TaMe}_2$ (93 G),²² where the odd electron is, presumably, located principally on tantalum. Similarly, $a_{31\text{P}}$ (29 G) is large.

The possibility of forming phosphorus anion radicals with bidentate ligands appears to be considerable, since electrochemical studies on triphenylphosphine and triphenylphosphine oxide demonstrate that their anion radicals can be produced

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via electrochemical reduction in aprotic solvents.⁴⁰ With the oxide, reduction in ethers with alkali metals produces an ESR signal characteristic of the reported species. Additional stabilization could be expected for bidentate ligands, but no data appear to be available.

Finally, in situations where one-electron oxidation produces 17-electron systems in formally common, stable, oxidation states, stable species can be formed without transfer of electron density to phosphorus. For example, the ^{31}P hyperfine in the ESR spectrum of $[\text{Mn}^{\text{II}}(\text{CO})_3(\text{P-P})\text{X}]^+$ is small and unresolved. However, the splitting arising from the metal hyperfine interaction is substantial.¹⁰

In summary, it can be concluded that the ability of bidentate phosphorus ligands to promote the oxidation of organometallic species to 17-electron systems in, formally, unusual oxidation states is widespread. This work establishes that this ability is not a feature of a particular metal or geometry. Stabilization may be attributable to the occurrence of an internal disproportionation, delocalizing electron density into the phosphorus orbitals, leaving the metal in a more common oxidation state.

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Registry No. $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]$, 73286-12-1; $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})\text{Br}$, 73274-59-6; $[(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Ta}(\text{DMPE})][\text{BF}_4]_2$, 73274-61-0; $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Cl}$, 61916-36-7; $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Br}$, 61966-89-0; $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{I}$, 65015-81-8; $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{CH}_3$, 61916-24-3; $\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{H}$, 50600-13-0; $\text{Ta}(\text{CO})_2(\text{DMDEPE})_2\text{Cl}$ (cis isomer), 65084-87-9; $\text{Ta}(\text{CO})_2(\text{DMDEPE})_2\text{Cl}$ (trans isomer), 65015-80-7; $\text{Nb}(\text{CO})_2(\text{DMPE})_2\text{Cl}$, 66507-17-3; $\text{Ta}(\eta^4\text{-naphthalene})(\text{DMPE})_2\text{Cl}$, 64367-79-9; $(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\text{DMPE})\text{PF}_6$, 73274-63-2; $(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{TaBr}_2$, 61202-67-3; $[\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Cl}]^+$, 73274-64-3; $[\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{Br}]^+$, 73274-65-4; $[\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{I}]^+$, 73274-66-5; $[\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{CH}_3]^+$, 73274-67-6; $[\text{Ta}(\text{CO})_2(\text{DMPE})_2\text{H}]^+$, 73307-15-0.

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Studies on the Rates of Isotopic Oxygen Exchange between Aqueated Molybdenum(V) and Solvent Water

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A method is described which allows precise isotopic analysis of the less labile oxygen atoms in the first coordination sphere of Mo(V) in aqueous media. Rapid conversion of $\text{Mo}^{\text{V}}(\text{aq})$, as generated by Hg^0 reduction of Mo(VI) in ca. 3 M HCl solution, to $\text{Mo}_2\text{O}_4\text{EDTA}^{2-}$ in labeled water shows no appreciable transfer of solvent oxygens to the product ion. Aqueated Mo(V), commonly referred to as $\text{Mo}_2\text{O}_4^{2+}$, is shown to contain 1.98 ± 0.03 slowly and 2.04 ± 0.06 rapidly exchanging oxygens (on the minute time scale) in agreement with the formula $\text{Mo}_2\text{O}_4^{2+}(\text{aq})$. The slowly exchanging oxygens are shown by Raman and IR ^{18}O shifts to be the bridging type having a $t_{1/2}$ of about 100 h at 40 °C while the yl-oxygens have a $t_{1/2}$ of about 4 min at 0 °C. Solvent in the coordination sphere exchanges much more rapidly. Some of the kinetic parameters and medium effects are evaluated and discussed.

Introduction

A precise knowledge of the structural nature and exchange behavior of aqueated metal ions is a prerequisite to future progress in reaction kinetics and mechanisms in aqueous media. However, our understanding of many of these ions has lagged

due to the difficulties involved in designing definitive experiments when the ligands are common to the solvent. Most structural information for ions in solution has been inferred from solid X-ray structures, and, fortunately, this has often been a reliable source, but, as more complete information is