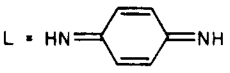
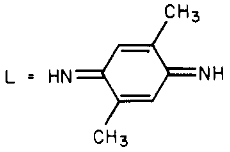
Table I. Visible and Near-Infrared Absorption Bands of $(NH_3)_5Ru\text{-}L\text{-}Ru(NH_3)_5{}^{5+}$

			
λ, nm	ϵ_{max}	λ, nm	ϵ_{max}
633	88000	643	44200
950, sh		1040, sh	
1355	1040	1400	670
1710	900	1770	800

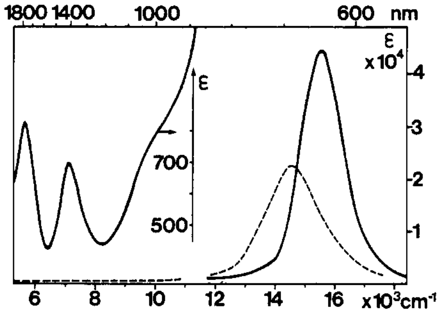


Figure 1. Electronic absorption spectrum (in D_2O) of **1** (R = CH_3, solid line) and its one-electron reduction product (broken line).

intensity. Prolonged action of Zn/Hg causes a steady intensity loss of the 686-nm band. The strong π backbonding of quinone diimine with the $Ru(NH_3)_5$ moiety is also illustrated by the ^1H NMR spectrum of its mononuclear complex with Ru(II). The splitting of the signals for the cis (3.54 ppm) and trans (6.53 ppm) ammonias which gauges this interaction is as large as 3 ppm compared to 1.10–2.10 ppm observed for other $Ru(NH_3)_5L$ species.[4]

In contrast to binuclear mixed-valence ruthenium complexes described so far[1] showing one intervalence band, the near-infrared solution spectrum of **1** exhibits three bands of medium intensity (Figure 1). An identical spectrum was also observed for very thin crystal plates of the $S_2O_6{}^{2-}$ salt of **1**. Intensity and bandwidth certainly eliminate their assignment to vibrational overtones. Spectroelectrochemical experiments[2] unambiguously classify these bands as an intrinsic property of **1**. The complexes produced by oxidation and reduction of **1** do not show any absorption band in this spectral region. The charge stoichiometry corresponds within 10% to a one-electron reaction for both processes, as verified by the coulometric evaluation of the corresponding cyclic voltammograms. We assign the three near-infrared bands of **1** to intervalence transitions, although a detailed energy level scheme cannot be specified at present. The appearance of three bands instead of one is tentatively attributed to an appreciable tetragonal distortion of the Ru coordination geometry, consistent with the ^1H NMR spectrum of pentaammine(quinone diimine)ruthenium(II). The narrow bandwidths of the order of 1000 cm^{-1} are indicative of considerable valence delocalization in **1**.

The two formal potentials corresponding to the oxidation and reduction of **1** are estimated from conventional cyclic voltammograms as 0.82 and 0.21 V (vs. NHE), respectively.[5] The comproportionation equilibrium is therefore markedly shifted to

$$Ru(II)\text{-}L\text{-}Ru(II) + Ru(III)\text{-}L\text{-}Ru(III) \rightleftarrows 2Ru(II)\text{-}L\text{-}Ru(III)$$

the side of the mixed-valence species **1**, the equilibrium constant K_{com} being 10^{10}. The onset of an irreversible wave in the cyclic voltammogram around −1 V is associated with the reduction of the ligand quinone diimine to 1,4-diaminobenzene.

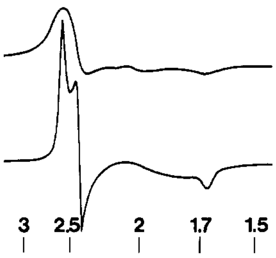


Figure 2. Powder EPR spectra of PF_6 salt of **1** (R = CH_3). Upper trace, 180 K; lower trace, 77 K.

We also have to consider the possibility that **1** is not a genuine mixed-valence complex but a Ru(II)–Ru(II) dimer bridged by a Wurster's blue type radical cation. A semiquinone anion bridged Ru(III)–Ru(III) complex is highly improbable considering the position and intensity of the visible absorption band. The EPR spectrum of either species, however, should consist of a signal close to $g = 2$, easily observable at room temperature.[6] A powder sample as well as a solution of **1** (R = CH_3) does not produce any EPR signal at room temperature.[7] We therefore can rule out the presence of an organic radical ion as the bridging ligand and confirm **1** as a mixed-valence complex. Below 200 K an EPR spectrum is observed, the signal line width considerably decreasing with decreasing temperature. The powder spectrum of the PF_6 salt of **1** at 77 K corresponds to $g_\parallel = 1.68$ and $g_\perp = 2.49$, the latter signal showing an additional rhombic splitting (2.56 and 2.42; Figure 2). A remarkable similarity is observed with the EPR spectrum of the Creutz–Taube complex, where $g_\perp = 1.33$ and $g_\parallel = 2.63$.[8] When the figures given in ref 8 for the orbital reduction factor ($k = 1$) and the spin–orbit coupling constant ($\lambda = -1050$ cm^{-1}) are used, a tetragonal splitting of 3000 cm^{-1} is estimated for **1**.

Acknowledgment. We thank Professor A. von Zelewsky, University of Fribourg, for measuring the EPR spectra. This work was supported by the Swiss National Science Foundation (Grant 2.427–0.79).

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Formation and Molecular Structure of Bis(η^5-cyclopentadienyl)bis(trifluorophosphine)titanium

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The similarity of PF_3 and CO as ligands was first noted by Chatt[1] in 1950 and subsequently confirmed by Wilkinson,[2] who synthesized the stable complex $Ni(PF_3)_4$ in 1951. Both PF_3 and CO are known to be weak σ donors and strong π acceptors toward transition metals, the stability of a PF_3–metal complex being attributed to strong d_π–d_π interaction between the ligand and the metal.[3-6]

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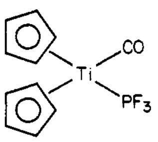
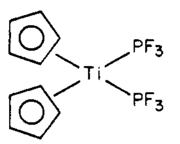
In spite of extensive research carried out on trifluorophosphine complexes of transition metals during the past 30 years,[3-7] isolable PF_3 derivatives of the early transition metals (groups 4B and 5B) are currently limited to two types of complexes of vanadium,[8,9] one complex of tantalum,[10] and one complex of zirconium,[11] all of which have been reportedly characterized by IR and ^1H NMR techniques. We now describe the formation and properties of the first trifluorophosphine derivatives of titanium and the results of a single-crystal X-ray diffraction investigation of one of the products. The latter study also represents the first crystallographic structural determination of a trifluorophosphine–early-transition-metal complex.[12]

Previous studies in our laboratory have shown that $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ are photochemically active, both in the presence and in the absence of suitable substrates such as phosphines or acetylenes.[14] In contrast, $Cp_2Ti(CO)_2$ did not appear to react by itself under photochemical conditions. To further investigate this phenomenon, we have prepared $Cp_2Ti(C^{18}O)_2$ (ν_{CO} 1934 and 1856 cm^{-1}) and have subsequently photolyzed it in hexane solution in the presence of $C^{16}O$. Carbon monoxide exchange to form $Cp_2Ti(C^{16}O)_2$ (ν_{CO} 1977 and 1899 cm^{-1}) is found to be complete in 20 min, and the intermediate species $Cp_2Ti(C^{16}O)(C^{18}O)$ (ν_{CO} 1959 and 1870 cm^{-1}) can also be identified by IR spectroscopy.

On the basis of these observations, the photolysis of $Cp_2Ti(CO)_2$ in hexane in the presence of excess PF_3 (sparged through the solution) has been investigated. Within 10 min, the carbonyl frequencies at 1977 and 1899 cm^{-1} are markedly decreased, and a strong new carbonyl band at 1932 cm^{-1}, assignable to $Cp_2Ti(CO)(PF_3)$ (**1**), is observed. Attempts to isolate **1** under these conditions have been hampered by the presence of $Cp_2Ti(CO)_2$ and $Cp_2Ti(PF_3)_2$ (**2**), both of which are difficult to separate from **1** by using chromatographic or crystallization techniques.[15] However, we have developed a more facile route to **1** involving the displacement of either PEt_3 or PPh_3 from the corresponding $Cp_2Ti(CO)(PR_3)$ (**3**, R = Et; **4**, R = Ph) complex.[16] Simply bubbling PF_3 through a hexane solution of **3** or a THF solution of **4** at room temperature over a 2-min period results in the formation of **1** as an air-sensitive red solid in nearly quantitative yield. As expected, the ^1H NMR spectrum of **1** in C_6D_6 exhibits a doublet (J_{H-P} = 3.5 Hz) at δ 4.59 due to coupling of the C_5H_5 protons with the ^{31}P nucleus, and the mass spectrum of **1** contains a molecular ion at *m/e* 294.



1



2

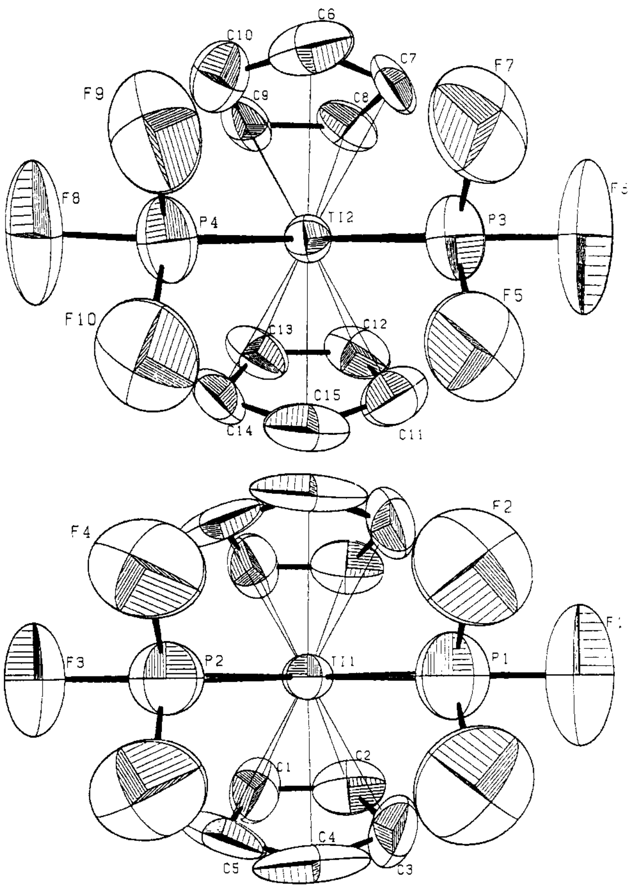


Figure 1. Views of the two crystallographically independent molecules of $Cp_2Ti(PF_3)_2$ (**2**). Average bond angle values of importance are centroid–Ti–centroid = 138°, centroid–Ti–P = 105°, and P–Ti–P = 87.7°.

When $Cp_2Ti(CO)_2$ is photolyzed in hexane solution in the presence of excess PF_3 for a 1.5-h period, no metal carbonyl bands can be detected, and the color of the solution changes from red to yellow. Filtration and removal of the solvent produce $Cp_2Ti(PF_3)_2$ (**2**) as an air-sensitive yellow solid in 78% yield. An analytically pure sample of **2** can be obtained by crystallization from hexane at −20 °C.[17] The ^1H NMR spectrum of **2** exhibits a triplet (J_{H-P} = 3.5 Hz) at δ 4.56, due to coupling of the C_5H_5 protons with the two equivalent ^{31}P nuclei. The IR spectrum of **2** (Nujol) contains a strong absorption at 850 cm^{-1} which we assign to a P–F stretching vibration.[6] The mass spectrum of **2** contains a molecular ion at *m/e* 354 as well as peaks at 266, 247, 197, and 178 assignable to $Cp_2TiPF_3^+$, $Cp_2TiPF_2^+$, Cp_2TiF^+, and Cp_2Ti^+ ions, respectively.

Complex **2** can be readily converted into $Cp_2Ti(CO)_2$ by bubbling CO through a hexane solution of **2** under nonphotochemical conditions. However, reactions of **2** with diphenylacetylene have thus far failed to yield an acetylene complex or a titanacycle, since only intractable products are obtained which appear to be paramagnetic.

In view of our interest in the chemistry and structures of decamethylmetallocene dicarbonyls of group 6B metals,[18] we have attempted the reaction of $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$ (**5**) and PF_3 under analogous photochemical conditions. Over the course of a 75-min photolysis period, no change in the metal carbonyl stretching frequency region could be detected. This result is consistent with the apparent enhanced photochemical stabilities of permethylated complexes such as **5** relative to their cyclopentadienyl counterparts.[18] However, we have subsequently found that photolysis of $(\eta^5\text{-}C_5Me_5)_2Ti(C^{18}O)_2$ (ν_{CO} 1900 and 1818 cm^{-1}) in hexane in the

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(15) It has been noted previously that separation of $M(PF_3)_x(CO)_{n-x}$ species is difficult due to their physical similarities.[3]

(16) Phosphine complexes **3** and **4** were prepared from reaction of $Cp_2Ti(CO)_2$ and an excess of the appropriate phosphine in refluxing hexane solution over a 24-h period. Compound **3**: IR (hexane) ν_{CO} 1864 cm^{-1}; ^1H NMR δ 4.75 (d, J_{H-P} = 1.5 Hz, C_5H_5). Compound **4**: IR (hexane) ν_{CO} 1864 cm^{-1}; ^1H NMR δ 4.67 (br s, C_5H_5).

(17) Anal. Calcd for $C_{10}H_{10}F_6P_2Ti$: C, 33.93; H, 2.85. Found: C, 34.02; H, 2.74.

(18) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* in press.

presence of $C^{16}O$ results in facile displacement of $C^{18}O$, with

$$(\eta^5\text{-}C_5Me_5)_2Ti(C^{18}O)_2 \xrightarrow[h\nu]{C^{16}O} (\eta^5\text{-}C_5Me_5)_2Ti(C^{16}O)_2 \xrightarrow[h\nu]{PF_3} (\eta^5\text{-}C_5Me_5)_2Ti(C^{16}O)(PF_3)$$

intermediate formation of $(\eta^5\text{-}C_5Me_5)_2Ti(C^{16}O)(C^{18}O)$ (ν_{CO} 1926 and 1835 cm^{-1}) and complete formation of $(\eta^5\text{-}C_5Me_5)_2Ti(C^{16}O)_2$ (ν_{CO} 1940 and 1858 cm^{-1}) in a 30-min period. These results imply that the carbonyl ligands in **5**, as in $Cp_2Ti(CO)_2$, are indeed photolabile; however, the reaction intermediate has a surprisingly much greater affinity for CO than for PF_3.

Crystals of **2** suitable for X-ray diffraction studies have been grown by slow sublimation at 50–55 °C (10^{-3} torr). An orange crystal of the compound was sealed in a thin-walled glass capillary. There are two crystallographically independent molecules in the unit cell.[19] One resides on a mirror plane, but the other possesses no site-imposed symmetry. There is, however, no apparent conformational difference between the two; Figure 1 presents a view of both molecules.

In the structure of $Cp_2Ti(CO)_2$,[20] a Ti^{2+} complex, the Ti–C(η^5) distances average 2.347 (13) Å, a value which is *less* than the 2.38 Å standard for complexes of Ti^{4+}.[21,22] This has been taken as evidence that the two d electrons reside in an orbital which is at least slightly bonding with respect to the titanium–cyclopentadienyl interaction. It is interesting to note that in the title compound **2** (also Ti^{2+}), the average of the Ti–C(η^5) lengths, 2.34 (1) Å, is similar. This structural observation is in accord with the fact that CO and PF_3 are similar in ligating ability.[1-3]

The Ti–P bond lengths range from 2.340 (6) to 2.349 (6) Å. Although there are no related compounds available for the purpose of comparison, two indirect estimates of a Ti–P bond of this sort may be obtained. First, the Ti–C(sp^3) length in $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$ is 2.20 Å.[23] Subtracting the C(sp^3) radius of 0.77 Å[24] affords an estimate of the Ti^{4+} radius of 1.43 Å in a Cp_2Ti fragment. The addition of the P(sp^3) covalent radius of 1.10 Å[24] yields an anticipated Ti–P length of ca. 2.53 Å. The second calculation is based on the Ti–Cl distance of 2.368 (4) Å in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2TiCl_2$.[25] If one corrects for the difference between the covalent radii of Cl and P, the projected Ti–P length is 2.48 Å. Thus, by the above estimates, the Ti–P bond distance in **2** is perhaps 0.15 Å less than expected.[26] It should also be pointed out that the Ti–CO length in $Cp_2Ti(CO)_2$ is also approximately 0.1 Å less than that in $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$ after a correction is made for the change in carbon atom hybridization. The similarity between the CO and PF_3 ligands, both capable of substantial back-bonding, is again underscored.

Acknowledgment. We are grateful to the National Science Foundation for support of this research program. We also thank Professor R. Holmes of the University of Massachusetts for a generous gift of PF_3.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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(19) The space group is *C2cm* with cell parameters of $a = 7.811$ (4), $b = 13.724$ (5), $c = 37.649$ (11) Å; $D_c = 1.75$ g cm^{-3} for $Z = 12$. Least-squares refinement on the basis of 1037 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.038$. Hydrogen atoms were included with fixed contributions and all nonhydrogen atoms were refined with anisotropic thermal parameters.

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Copper Site of Molluscan Oxyhemocyanins. Structural Evidence from X-ray Absorption Spectroscopy

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Knowledge of the molecular architecture around the copper atoms in the "type 3" site of hemocyanins is of importance in understanding how these proteins reversibly bind dioxygen. Analysis of the extended X-ray absorption fine structure (EXAFS) has proven to be useful in the structural elucidation of specific metal sites in metalloproteins under noncrystalline conditions.[1] Indeed, hemocyanin was among the first metalloproteins studied by using EXAFS. This study revealed only low *Z* atoms (nitrogen or oxygen) in the first coordination sphere and demonstrated that a binuclear copper interaction, if present, had a separation between the two metals of greater than about 2.7 Å.[2] More recently, Spiro and co-workers[3] reported an EXAFS study on *Busycon canaliculatum* hemocyanin. Their work showed four or five low *Z* atoms coordinated to each copper in the oxygenated form with a Cu–Cu separation of 3.67 Å. Their proposed model consists of two copper atoms each bound to three histidine ligands and bridged by a bound peroxide and an atom from a protein ligand. We report here our EXAFS analysis by using imidazole group fitting[4] on the oxy forms of *Megathura crenulata* and the α and β components of *Helix pomatia* hemocyanin. This EXAFS reveals only two imidazoles and two low *Z* atoms per copper. Using the EXAFS, as well as the K absorption edge and other spectroscopic data, we propose a model for the binuclear type 3 copper site in which the copper atoms are separated by 3.55 Å. Comparison of the results on oxyhemocyanins from two different species is also discussed.

Hemocyanin is a copper-containing protein which functions as a dioxygen carrier in molluscs and arthropods. The smallest functional subunits, with a molecular weight of ca. 50 000 for molluscs and 75 000 for arthropods, contain two copper atoms and bind one molecule of dioxygen reversibly. Many studies have been aimed at elucidating the structure of the active site.[5] Results from resonance Raman spectroscopic studies[6] have established that in oxyhemocyanin the bound oxygen is in the form of peroxide (O_2^{2-}). On the basis of near-UV and visible absorption spectroscopy, sulfhydryl groups[7,8] and imidazole groups[8,9] have been suggested to be copper ligands. Acid–base titration studies[10] and photooxidative studies[11] support the binding of imidazole groups

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