A Carbon-Free Sandwich Complex $[(P_5)_2Ti]^{2-}$

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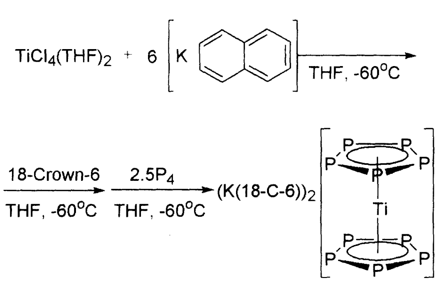
Reactions of highly reduced titanium complexes with white phosphorus, P_4, at or below 25°C yielded brown to deep red-brown salts of the first entirely inorganic metallocene, $[(\eta^5\text{-}P_5)_2Ti]^{2-}$ (1). Like ferrocene and other carbon-based metallocenes, the structure of 1 has parallel and planar five-membered rings symmetrically positioned about the central metal atom. Despite its electron-deficient (16 electron) and formally zerovalent titanium character, salts of 1 are highly stable toward heat and air, both in solution and in the solid state. Computational studies show that the pentaphosphacyclopentadienyl unit, P_5, functions as an unusually effective acceptor ligand, and this results in substantial stabilization of 1.

The first bis-η^5-cyclopentadienyl metal complex, $(C_5H_5)_2Fe$, was reported just 50 years ago (*1*, *2*). Termed "ferrocene" to emphasize the notable similarities with benzene, this sandwich structure shares the thermal stability of arenes and their ability to undergo facile electrophilic substitution reactions (*3*). Ferrocene and analogous organometallic compounds called metallocenes have found many applications as synthetic reagents, olefin polymerization catalysts, and building blocks for new materials (e.g., polyferrocenes) (*4*, *5*). The field has expanded to include heterocyclic analogs of $C_5H_5^-$, abbreviated Cp^- (*6*). In particular, the replacement of CH fragments in metallocenes by electronically equivalent (isolobal) P atoms (*7*) has led to the synthesis of penta- and hexa-phosphametallocenes of several transition metals, whose properties are often markedly different from those of their all-carbon analogs (*8–16*). Prior electrochemical, photoelectron spectroscopic, and computational studies have established that the superior acceptor abilities of polyphosphacyclopentadienide ligands compared with Cp^- are responsible for many of these differences (*12–16*). The all-phosphorus analog of Cp^-, pentaphosphacyclopentadienide P_5^-, has been prepared in solution with alkali-metal counterions (*17*) and isolated in mixed-sandwich complexes, Cp^xMP_5 (M = Fe, Ru; Cp^x = C_5Me_5 or C_5Me_4Et) and a few related species (*18*). Computational studies have suggested that P_5^- is almost as aromatic as Cp^- or benzene (*19*, *20*). Attempts to prepare decaphosphametallocenes were first described by Baudler 10 years ago (*21*). We now report the synthesis and the characterization of such a species, $[(\eta^5\text{-}P_5)_2Ti]^{2-}$, a carbon-free metallocene.

Reactions of white phosphorus, P_4, with low-valent transition-metal complexes have led to a wide variety of compounds containing P_n (n = 1 to 8) ligands (*22*), but only one involving Ti has been described previously (*23*). Reduction of $TiCl_4(THF)_2$ (THF = tetrahydrofuran) by 6 equiv. of potassium naphthalenide in THF at −60°C, followed by addition of 2 equiv. of 18-Crown-6, provides a highly reactive naphthalene-stabilized titanate(2−) (*24*). As shown in Scheme 1, the reaction of this intermediate with 2.5 equiv. of P_4 provides a brown powdery solid containing $[K(18\text{-Crown-}6)]_2$**1** (*25*). This remarkable conversion gives a very high yield (up to 77%) of a P_5-metal complex for a direct reaction involving white phosphorus. Also, dianion **1** is notable, because no anionic η^5-P_5 metallocene containing a ligand has been previously isolated (*26*) and no carbon-based metallocene dianion, i.e., $[Cp_2M]^{2-}$, has been reported.



Low-temperature cation-exchange reactions of $[K(18\text{-Crown-}6)]_2$**1** with tetraphenylphosphonium chloride or bis(triphenylphosphine)iminium (PPN) chloride provided crystalline $(Ph_4P)_2$**1** and $(PPN)_2$**1** in 15% and 20% yields, respectively, after purification. These salts of **1** were only sparingly soluble in tetrahydrofuran, but quite soluble in pyridine, acetonitrile, dimethylsulfoxide, dimethylformamide, and acetone; solutions were thermally stable indefinitely at 20°C. Salts containing **1** were diamagnetic in solution by the Evans method (*27*) and gave sharp ^{31}P–nuclear magnetic resonance (NMR) peaks, essentially independent of cation and solvent (121 MHz, 20°C): 60 to 63 parts per million (ppm). Also, solid-state NMR spectra of **1** showed similar ^{31}P shifts, e.g., 68.6 ppm for the PPN^+ salt (162 MHz, 20°C), thus indicating the close relation of structures of **1** in solution and in the solid state. Single-crystal x-ray structures of the Ph_4P^+ and PPN^+ salts were determined and showed identical anions (*28*). Only the former structure will be discussed here. Structural characterization of $(Ph_4P)_2$**1** revealed two identical, unexceptional tetraphenylphosphonium cations symmetrically and well separated from the decaphosphatitanocene dianion (Fig. 1). Because the Ti in **1** lies on a crystallographic twofold axis, there are two symmetry-related and identical P_5 rings. The molecular structure of **1** (Fig. 1) depicts the parallel P_5 rings [$<(P_{5(\text{centroid})}\text{-Ti-}P_{5(\text{centroid})})$ = 178.5(1)°] symmetrically positioned about the central Ti atom.

Although the P_5 and cyclopentadienide rings are staggered in the structurally characterized Cp^xMP_5 (M = Fe, Ru) mixed-sandwich complexes (*22*), the two P_5 rings are eclipsed in **1**. The average P-P bond distance [2.154(9) Å], intermediate between P-P single (2.21 Å) and P=P double (~2.02 Å) bond lengths (*29*), is significantly longer than the experimental P-P distances for Fe and for Ru mono-P_5 complexes (2.07 to 2.12 Å) (*18*, *30*) and computed for P_5^- (2.08 to 2.12 Å) (*20*, *31*). However, the metal-P_5(center) separation in **1** of 1.797(1) Å is about 0.2 Å longer than the corresponding distances in Fe mono-P_5 complexes (1.52 to 1.58 Å) (*18*, *30*). The longer Ti-P_5 separation can be expected because transition metal–ring center distances in metallocenes gradually decrease from left to right in the periodic table (*13*). Finally, the average Ti-P distances of 2.56 (1) Å are within the range previously observed for Ti-P compounds (*32*) and for a hexaphosphatitanocene (*13*).

Density functional computations using the Perdew-Wang exchange and correlation functionals (*33*, *34*) as modified by Adamo and Barone (*35*) (*m*PW1PW91) and the 6-31+G* basis set (*36*) were carried out to further elucidate the nature of **1** in comparison with related species. Computed gas-phase molecular geometries and ^{31}P chemical shifts for **1** and several other known metallocenes incorporating a single P_5 ligand were in good agreement with available experimen-

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tal values, thereby validating the theoretical model. Analysis of the Kohn-Sham orbitals (*37*) for **1** indicates that there are critical differences in the nature of the organic versus inorganic metal-ligand bonding as illustrated in Fig. 2. The ligand π orbitals of P_5 are lower than those of Cp. Consequently, the strongest P_5 π interactions involve the empty ligand e_2' and the filled metal e_2' orbitals. In contrast, the strongest Cp interactions involve the filled ligand and the empty metal e_1'' orbitals. Thus, Cp serves more as a donor and P_5 as an acceptor. The strong stabilization of the lowest e_2 orbital set in $(P_5)_2M$ creates a substantial e_2-a_1 energy gap, and 16-electron complexes, like **1**, are predicted to be ground-state singlets by large margins. As a result, the two lowest energy triplet states of **1**, each of which derives from a different $e_2 \rightarrow a_1$ promotion and undergoes Jahn-Teller distortion, are predicted to be 23.7 kcal mol^{-1} higher in energy than the ground-state singlet. This is in sharp contrast to the analogous situation with Cp as a ligand, where, for example, Cp_2Cr is known to be a ground-state triplet owing to a much smaller e_2-a_1 splitting of the metallocene hybrid orbitals (*38*).

The ring rotation barriers about the metal in **1** and the Cp-based metallocenes are markedly different: The computed barrier is 7.8 kcal mol^{-1} for **1** but only 1.4 kcal mol^{-1} for ferrocene, where the latter barrier is in good agreement with the experimental value of 0.9 ± 0.3 kcal mol^{-1} (*39*). Because rotational barriers of π-complexed ligands tend to increase as metal π-donation (backbonding) becomes more important in a complex (*40*), the relatively large value computed for **1** is another indication that P_5^- functions as a good acceptor ligand in this complex.

Even though **1** is a 16-electron species and therefore formally isovalent with the Group 6 metallocenes, it is far less chemically reactive. Thus, whereas Cp_2M (M = Cr, Mo, W) readily react with carbon monoxide to form carbonyl complexes $[Cp_2M(CO)]$ and $[Cp_2M(CO)_2]$ and associated species (*41*), solutions of $[K(18\text{-Crown-6})]_2$**1** were inert toward 2,6-dimethylphenylisocyanide, $P(OCH_3)_3$, or ^{13}CO (as ascertained by ^{31}P-NMR and ^{13}C-NMR spectra). Furthermore, solutions of $[K(18\text{-Crown-6})]_2$**1** were found to be stable toward pure dioxygen for weeks, and only slow decomposition occurred in wet pyridine. Crystalline samples of $(Ph_4P)_2$**1** and $(PPN)_2$**1** remained unchanged in air after several hours. Both are also quite thermally stable, melting (with decomposition) at 213° to 215°C and 319° to 323°C, respectively. Although mixed-sandwich η^5-P_5–cyclopentadienyl metal complexes (*18*) and hexaphosphatitanocene (*13*) were reported to be about as chemically reactive as their carbon-based analogs, such low reactivity for a formally Ti(0) complex is unprecedented. For example, bis(η^6-benzene)Ti(0) was reported to be "extremely air sensitive" (*42*), as are all other known Ti(0) compounds (*43*).

The highly inert nature of **1** is very likely due to both electronic and steric effects. As mentioned above, the strong acceptor ability of ligated η^5-P_5 rings will facilitate removal of considerable electron density from the Ti center and render the latter much less electron rich or strongly reducing than previously known Ti(0) complexes. Indeed, the nonexistence of carbon-based metallocene dianions, such as $[Cp_2Ti]^{2-}$ or $[Cp_2Cr]^{2-}$, emphasizes the special role of P_5^- in stabilizing **1**. The Ti center in **1** may be a sufficiently weak π donor that it prevents reactions of **1** with good acceptor ligands such as CO, aryl isocyanides, and organophosphites, at least under our experimental conditions. However, the appreciably shorter ring(center)-ring(center) distance in **1** (3.6 Å) than the corresponding distances in carbon-containing titanocenes (4.0 to 4.2 Å), the larger ring size of P_5 versus Cp, and the presence of lone pairs of electrons on the P atoms in **1** should also sterically inhibit attack at the Ti center.

Initial reactivity studies show that the P_5^- rings in **1** are somewhat labile toward certain bases. For example, prolonged exposures of $[K(18\text{-Crown-6})]_2$**1** solutions in pyridine to 1,2,3,4,5-pentamethylcyclopentadienyl potassium (Cp*K) or 1,4,7-triazacyclononane at room temperature led to displacement of P_5^- from the metal center, as evidenced by the appearance of an intense signal at 468 ppm in ^{31}P-NMR, attributed to P_5^-– alkali metal salts by Baudler and co-workers (*17*, *44*). These results suggest that **1** may serve as the first available isolable source of P_5^- in chemical reactions.

Previous attempts to prepare and characterize neutral, homoleptic all-phosphorus metallocenes "led, without exception, to high molecular weight solids" (*21*). Our success in obtaining such a complex in the form of a charged species suggests that electrostatics

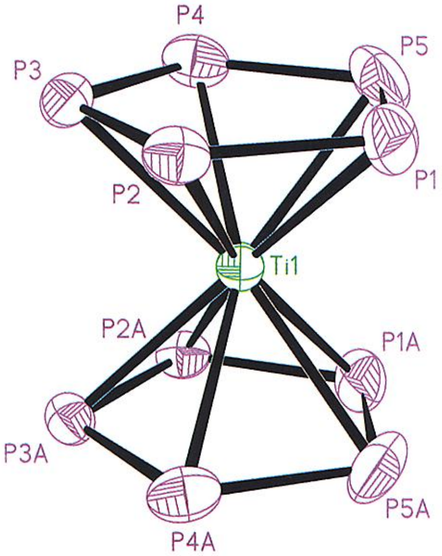

Fig. 1. Molecular structure of **1**, 50% thermal ellipsoids. Selected bond distances (Å): P1-P2, 2.1608(11); P2-P3, 2.1477(9); P3-P4, 2.1469(10); P4-P5, 2.1500(12); P5-P1; 2.1661(13); P1-Ti, 2.5617(8); P2-T1, 2.5443(7); P3-Ti, 2.5753(8); P4-Ti, 2.5811(8); P5-Ti, 2.5697(8).

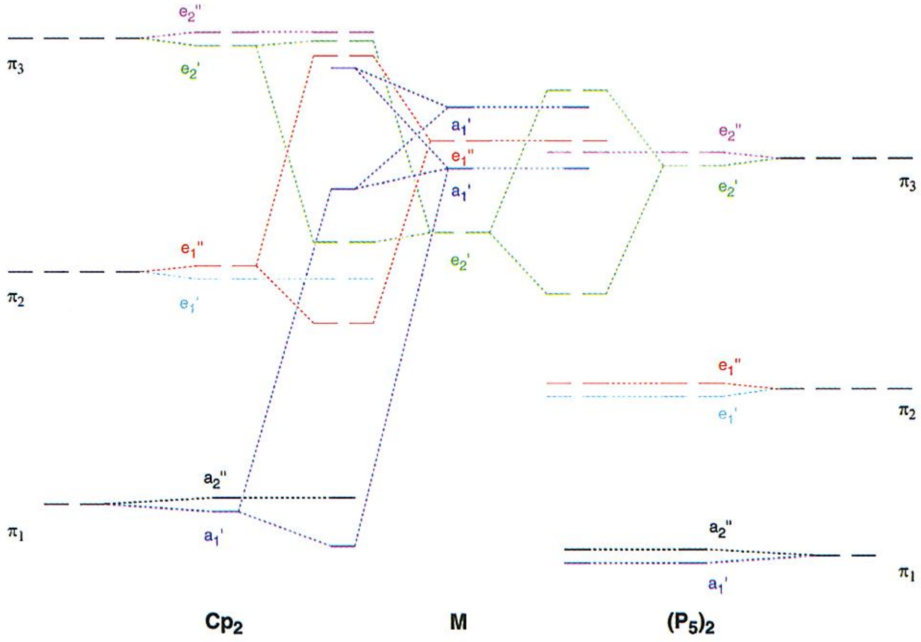

Fig. 2. Qualitative interaction energy diagram for metal d orbitals interacting with Cp_2 and $(P_5)_2$ ligand systems. Symmetry labels are from the D_{5h} point group.

may also play an important role in the stabilization of monomers containing $[(P_5)_2M]^z$ units. On this basis, it seems possible that a wide variety of other charged decaphosphametallocenes and related carbon-free sandwich complexes (*45*) may be accessible species.

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Aerosol Effect on Cloud Droplet Size Monitored from Satellite

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Aerosol concentration and cloud droplet radii derived from space-borne measurements are used to explore the effect of aerosols on cloud microphysics. Cloud droplet size is found to be largest (14 micrometers) over remote tropical oceans and smallest (6 micrometers) over highly polluted continental areas. Small droplets are also present in clouds downwind of continents. By using estimates of droplet radii coupled with aerosol load, a statistical mean relationship is derived. The cloud droplet size appears to be better correlated with an aerosol index that is representative of the aerosol column number under some assumptions than with the aerosol optical thickness. This study reveals that the effect of aerosols on cloud microphysics is significant and occurs on a global scale.

Aerosols may reduce the degree of Earth global warming resulting from the increase of greenhouse gases in the atmosphere (*1*, *2*). They directly impact the radiative balance of Earth through a net increase of its albedo, particularly over the oceans (*3*, *4*). Aerosols can also act as cloud condensation nuclei (CCN), increasing the number of droplets in clouds, which tends to decrease the mean droplet size and may increase the cloud albedo (*5*), depending on the aerosol absorption and cloud optical thickness (*6*). This process, referred to as the "Twomey effect" or the "first indirect" aerosol radiative forcing, has a net cooling effect on climate. A direct demonstration of the aerosol effect on cloud albedo was provided by the observation of lines of larger reflectance in cloud fields identified as tracks of ship exhaust (*7*). Indirect observations of this effect can also be made by comparing cloud droplet size and aerosol concentration. Cloud droplet effective radii were derived by using global scale AVHRR (advanced very high resolution radiometer) measurements (*8*). The results of a global application (*9*) indicate a contrast in cloud droplet size of about 2 μm over land and ocean surfaces, as well as a hemispheric contrast of 1 μm, both of which support the Twomey hypothesis. Similar patterns of the aerosol optical thickness and the cloud droplet effective radius, derived from AVHRR measurements, have been observed over the oceans (*10*). Cases of reduced droplet radii and suppression of rain—the second indirect aerosol effect—in areas of high aerosol load were identified on satellite imagery (*11*, *12*). Furthermore, several in situ measurements have shown a relationship between the aerosol concentration and the cloud droplet size distribution (*13*–*15*).

The polarization and directionality of the earth reflectances (POLDER) instrument (*16*) is well suited for assessing the Twomey hypothesis globally, because its measurements provide a unique opportunity to measure cloud droplet effective radius (hereafter referred to as CDR) (*17*), as well as aerosol loading (*18*), over both land and ocean surfaces. The POLDER radiometer was launched aboard the Advanced Earth-Observing Satellite (ADEOS) in August 1996. Continuous monitoring of the solar radiation reflected by the earth, including its polarization and directional signatures, started on 30 October 1996, and ended on 30 June 1997, with the unexpected failure of the satellite solar panel. Monthly maps were generated of an

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