Low-Valent Titanium Bis(phospholyl) Chemistry: A Configurationally Stable Chiral Phosphatitanocene

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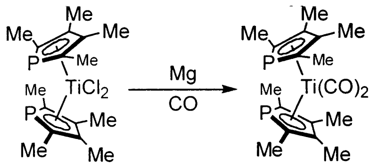
The first example of a low-valent phosphatitanocene has been prepared and structurally characterized, and a chiral Ti(II) phosphametallocene was prepared and was found to have a significantly higher barrier to isomerization than the Ti(IV) analogue. Descriptions of the molecular orbitals of the two complexes offer an explanation of the difference.

Introduction

Heterocyclic π-ligands are of significant interest in the continuing development of transition metal ligands, and phospholyl anions ($C_4R_4P^-$), analogues of the cyclopentadienyl anion ($C_5R_5^-$), have been receiving much attention.[1,2] Reports of the synthesis of phospholyl transition metal complexes have been summarized in several reviews.[3] The phosphatitanocenes and phosphazirconocenes in the +4 oxidation state have been known for more than two decades.[4] They have been structurally characterized, providing unequivocal evidence for the bonding modes of these complexes.[5] While the low-valent chemistry of bis(cyclopentadienyl) complexes of the Ti triad is rich, plentiful, and well-documented,[6,7] reports of the corresponding low-valent chemistry of the bis(phospholyl) complexes have begun to appear only recently.[8,9] We report here the first examples of bis(phospholyl)Ti(II) complexes.

Results and Discussion

The achiral Ti(II) complex **1** was prepared in analogy with established procedures for the reduction of metallocenes. Mathey and co-worker's recently reported Mg reduction conditions for phosphazirconocenes proved most productive for Ti also.[9] (η^5-$C_4Me_4P)_2TiCl_2$ was prepared in situ, according to literature procedures from 1-(trimethylstannyl)-2,3,4,5-tetramethylphosphole, and was reduced using Mg powder under an atmosphere of CO at 40 °C (eq 1). The desired complex **1** was obtained



(1)

in 39% yield. Titanium(II) complex **1** was characterized by IR and NMR spectroscopy (^1H, ^{31}P, and ^{13}C). The CO stretches are readily apparent in the IR spectrum (1959, 1900 cm^{-1}), and satisfactory elemental analysis was obtained.

X-ray quality crystals of **1** were grown from a toluene solution at −35 °C, and the red needles were used for the structural analysis.[10] An ORTEP plot of Ti(II) complex **1** is presented in Figure 1 with pertinent structural details. This structure is related to the Zr analogue reported by Mathey,[9] but it lacks crystallographic symmetry. The dihedral angle between the P atoms (P−Ctr−Ctr−P, Ctr = centroid) is approximately 180°, which results in a staggered conformation of the rings, unlike the corresponding Cp* analogue that has the rings in an eclipsing conformation.[11] The staggered conformation produces an antiparallel arrangement of the P-lone pair vectors, resulting in dipole minimization.

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(1) For recent examples of other heterocyclic π-ligands see: Boratabenzene: (a) Ashe, A. J.; Al-Ahmad, S.; Fang, X. D.; Kampf, J. W. *Organometallics* **2001**, *20*, 468−473. (b) Ashe, A. J.; Al-Ahmad, S.; Fang, X. G. *J. Organomet. Chem.* **1999**, *581*, 92−97. (c) Bazan, G. C.; Cotter, W. D.; Komon, Z. J. A.; Lee, R. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1371−1380. (d) Rogers, J. S.; Bu, X. H.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 730−731. (e) Lee, B.; Wang, S.; Putzer, M.; Bartholomew, G.; Bu, X.; Bazan, G. *J. Am. Chem. Soc.* **2000**, *122*, 3969−3970. (f) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 8176. Borabenzene: (g) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1997**, *16*, 1501−1502.

(2) For a recent review of chiral phospholyl chemistry see: Ganter, C. *J. Chem. Soc., Dalton Trans.* **2001**, 3541−3548.

(3) For reference to recent reviews see: (a) Ashe, A. J.; Al-Ahmad, S. *Adv. Organomet. Chem.* **1996**, *39*, 325−353. (b) Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1−52. (c) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy. From Organophosphorus to Phospha-Organic Chemistry*; John Wiley & Sons: New York, 1998.

(4) The first spectroscopically characterized complexes were reported by Meunier, P.; Gautheron, B. *J. Organomet. Chem.* **1980**, *193*, C13−C16.

(5) For well-characterized examples see: (a) Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1988**, 770−771. (b) Nief, F.; Mathey, F.; Ricard, L. *Organometallics* **1988**, *7*, 921−926. (c) Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **1989**, *8*, 1473−1477.

(6) For reviews see: (a) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1−50. (b) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1984**, *24*, 1−39. (c) Sikora, D. J.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.* **1986**, *25*, 317−379. (d) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058.

(7) For other recent low-valent chemistry of the Ti triad with heterocyclic ligands see: (a) Boroles: Kiely, A. F.; Nelson, C. M.; Pastor, A.; Henling, L. M.; Day, M. W.; Bercaw, J. E. *Organometallics* **1998**, *17*, 1324−1332. (b) Germoles: Dysard, J. M.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 3097−3105. (c) Boratabenzenes: Ashe, A.; Al-Ahmad, S.; Kampf, J. *Organometallics* **1999**, *18*, 4234−4236.

(8) Hollis, T. K.; Wang, L.-S.; Ahn, Y. J.; Freeman, W. P. *Division of Inorganic Chemistry, Abstracts of Papers of the American Chemical Society* **2001**, *222*, 540.

(9) Buzin, F.-X.; Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **2002**, *21*, 259−263.

(10) Crystal data for $C_{18}H_{24}O_2P_2Ti$, **1**: $M = 382.21$, monoclinic, $C2/c$, $a = 16.018(3)$ Å, $b = 7.4328(13)$ Å, $c = 32.774(5)$ Å, $\alpha = 90°$, $\beta = 102.498(4)°$, $\gamma = 90°$, $Z = 8$, $T = 223(2)$ K, $d_{calcd} = 1.333$ Mg/m^3, $F(000) = 1600$, μ(Mo Kα) = 0.623 mm^{-1}, λ(Mo Kα) = 0.71073 Å, 3886 independent reflections measured, R1 = 0.0479 ($I > 2.00\sigma(I)$), wR(F^2) = 0.1323 (all data).

(11) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265−1267. See also the reviews listed in ref 6 and references therein.

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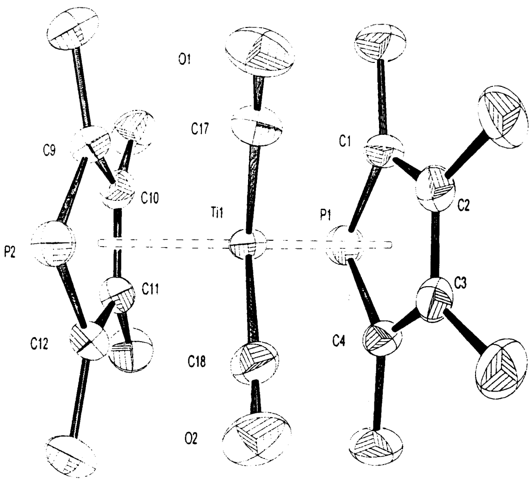

Figure 1. ORTEP plot of the monoclinic Ti(II) complex bis(η^5-2,3,4,5-tetramethylphospholyl)titanium dicarbonyl, **1**, shown at 50% probability thermal ellipsoids. Selected structural parameters: Ti−Ctr = 2.066, 2.090 Å; Ti−C(O) = 2.040, 2.044(3) Å; Ti−P = 2.5611(10) Å, 2.5825(11) Å; C−O = 1.150, 1.147(4) Å; Ctr−Ti−Ctr = 144°; (O)C−Ti−C(O) = 89°; P−Ctr−Ctr−P = 179.1°.

Table 1. Comparison of $\nu(CO)_{av}$ and Structural Parameters for $L_2M(CO)_2$ Bent Metallocenes (TMP = 2,3,4,5-tetramethyl phospholyl)

L	$\nu(CO)_{av}$[a]	OC−M−CO[b]	Ctr−M−Ctr[b]
		$L_2Ti(CO)_2$	
Cp[c]	1938	87.9	138.6
TMP[d]	1930	88.7	144.0
Cp*[c]	1899	83.3	147.9
		$L_2Zr(CO)_2$	
Cp[e]	1930	89.2	143.4
TMP[f]	1934	91.3	143.9
Cp*[e]	1900	86.3	147.4

[a] cm^{-1}. [b] deg. [c] See ref 6c and references therein. [d] This work. [e] Ref 11. [f] See ref 9.

The Ti−P distance is greater for the P atom bisecting the carbonyl groups (2.5825(11) vs 2.5611(10) Å). The Ti−Ctr distances for the Ti(II) complex are 2.066 and 2.090 Å. The phospholyl ring with the shorter Ti−Ctr distance has the P atom at the narrow side of the metallocene wedge, and the one with the P atom bisecting the (O)C−Ti−C(O) angle has the longer Ti−Ctr distance. The Ti−Ctr distance is expected to decrease for the Ti(IV) analogue since the metal center is formally more electron deficient. But, the Ti−Ctr distances in the closest Ti(IV) analogue for which a crystal structure has been reported, (3,4-dimethylphospholyl)$_2$TiCl$_2$, are on average 2.154 Å compared to 2.088 Å for the Ti(II) complex.[5c] Part of this increase in the Ti−Ctr distance for the Ti(IV) analogue can be attributed to increased steric repulsion between the phospholyl ligand and Cl compared to the corresponding interaction with CO (covalent radii: C(sp) = 0.603 Å vs Cl = 0.99 Å).[12] In addition, there is a bonding interaction between the filled metal orbital and the ligand π*-orbital Ti(II) complex (vide infra).

The CO stretching frequencies for the Ti(II) complexes of Cp, Cp*, and (η^5-C_4Me_4P) provide a means of comparing the donor ability of each ligand. The CO stretching frequencies in hexane found for (η^5-C_4Me_4P)$_2$Ti(CO)$_2$ (1959, 1900 cm^{-1}) are between those reported for Cp$_2$Ti(CO)$_2$ (1977, 1899 cm^{-1}) and Cp*$_2$Ti(CO)$_2$ (1940, 1858 cm^{-1}).[11] The symmetric CO stretching frequency observed for the phosphametallocene is halfway between that of Cp and Cp* (1940 < 1959 < 1977 cm^{-1}), while the asymmetric stretch is almost identical to that of Cp (1899 ≈ 1900 > 1858 cm^{-1}). Considering the average of the symmetric and asymmetric stretches for each of the complexes, the order observed is Cp*, 1899 cm^{-1} < (η^5-C_4Me_4P), 1930 cm^{-1} < Cp, 1938 cm^{-1}. These observations lead to the conclusion that the tetramethylphospholyl ligand (TMP = (η^5-C_4Me_4P)) is intermediate between Cp and Cp* in electron-donating character (π-basicity). This conclusion is different from that recently reported for the Zr analogue where (η^5-$C_4Me_4P^-$) was found to be a weaker donor than Cp.[9]

The difference in apparent donor ability of the tetramethylphospholyl (TMP) ligand relative to Cp and Cp* in Ti versus Zr complexes presents an intriguing conundrum. The two phosphametallocenes are isoelectronic and, in gross features, isostructural. Yet, examination of the subtle structural differences allows an adequate explanation to be offered, which is analogous to that recently offered for the *ansa*-effect in the monumental paper by Parkin, Bercaw, Green, Keister, and co-workers.[13] Presented in Table 1 is a comparison of $\nu(CO)_{av}$ for the Ti and Zr complexes of Cp, TMP, and Cp* alongside the key structural parameters (O)C−M−C(O) and Ctr−M−Ctr. If the change in (O)C−M−C(O) angle was the dominate factor contributing to the stretching frequency differences, then the angle for the TMP complexes should be at different positions relative to Cp and Cp* for the Ti versus Zr series. The observed (O)C−M−C(O) angles follow the same order in Ti and Zr (TMP > Cp > Cp*). In contrast to the OC−M−CO structural parameters, the Ctr−M−Ctr angle follows a different pattern in the Ti and Zr series, a pattern that correlates with the stretching frequencies. The Ctr−M−Ctr angle increases for the Ti complexes in the order Cp < TMP < Cp*, which is inversely correlated with the stretching frequency, whereas the Ctr−M−Ctr angles for the Zr complexes are observed to vary such that Cp ≈ TMP < Cp*, and the $\nu(CO)_{av}$ frequencies are inversely correlated with the angle (Cp*, 1900 cm^{-1} < TMP, 1934 cm^{-1} ≈ Cp, 1930 cm^{-1}).

Bent metallocene dicarbonyl $\nu(CO)_{av}$ stretching frequencies have been correlated recently with the Ctr−M−Ctr angle for a large number of zirconocene dicarbonyl complexes. The explanation offered was that the overlap, and therefore the back-bonding, between the metal orbitals and the "cyclopentadienyl ligand acceptor orbital" improves as the Ctr−M−Ctr angle decreases.[13] The increased back-bonding to the cyclopentadienyl ligand decreases back-bonding to the CO ligand, resulting in higher frequency CO stretches for more bent complexes. The data for the tetramethylphospholyl complexes of Ti and Zr are consistent with this explanation. The differences between the apparent donor ability of TMP relative to Cp and Cp* in the Ti and Zr series

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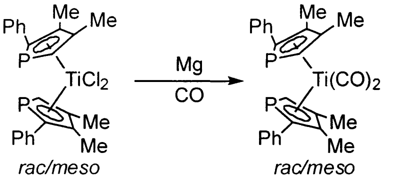
(12) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry*, 3d ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

(13) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525−9546.

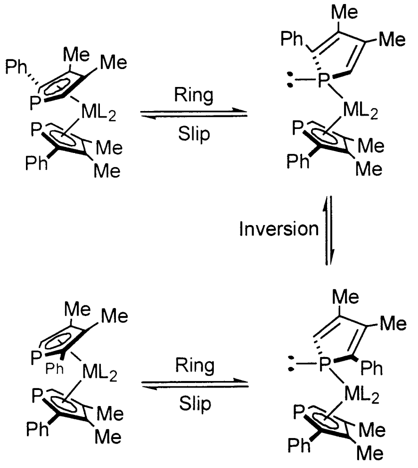
correlate with the Ctr−M−Ctr angle. The apparent electron-donating ability of the TMP ligand relative to Cp and Cp* has been found to vary in the closely related analogues ($(\eta^5\text{-}C_4Me_4P)_2Zr(CO)_2$ and $(\eta^5\text{-}C_4Me_4P)_2Ti(CO)_2$. The source of the difference is attributable to subtle geometric changes in the Ctr−M−Ctr angle that change the energy of the a_1 (HOMO) orbital. Finally, the change in apparent ligand donor capacity is not due to a change in the geometry of the TMP complexes, but is due to a large Ctr−M−Ctr angle for $Cp_2Zr(CO)_2$ (Table 1). The large Ctr−M−Ctr angle for $Cp_2Zr(CO)_2$ produces decreased back-bonding to the Cp ligand and increased back-bonding to the CO, which results in an "anomalously" low $\nu(CO)_{av}$ stretching frequency (1930 cm^{-1}). This geometric flexibility of organometallic complexes makes overgeneralization regarding ligand donor ability and substituents effects in organometallic complexes easy. The comparisons presented herein suggest that generalization even between very closely related isoelectronic complexes (Ti vs Zr) can fail.

The influence of metal oxidation state on the *rac*/*meso* isomerization of chiral phosphametallocenes is of fundamental interest. Following up our initial report of the facile thermal isomerization of chiral bis(phospholyl) complexes of Zr,[14] we have recently reported the activation parameters for the isomerization process in a Ti(IV) analogue based on variable-temperature NMR.[15,16] The activation barrier for the isomerization of *rac*/*meso*-$(\eta^5\text{-}C_4Me_2(Ph)HP)_2TiCl_2$ was found to be $\Delta G^\ddagger = 11.5$ kcal/mol. We undertook the preparation of chiral analogues of **1**, as outlined in eq 2, to prepare the chiral bis(phospholyl)Ti(II) dicarbonyl complex **2**. This Ti(II) complex has two distinct resonances in the ^{31}P NMR spectrum (4.13, −13.6 ppm, ratio 24:76 in C_6D_6) consistent with *rac* and *meso* isomers. The ^1H NMR spectrum also revealed the expected duplications due to *rac* and *meso* isomers. The IR spectrum shows two CO stretches at 1971 and 1914 cm^{-1} for an Et_2O cast film. In hexane solution, the IR spectrum at 0.5 cm^{-1} resolution contains five CO stretches (1992, 1981, 1975, 1931, and 1918 cm^{-1}) with a shoulder on the 1981 signal.[17] The observation of two sharp signals in the ^{31}P NMR spectrum of complex **2** is distinct from the Ti(IV) dichloro analogue, which has a broadened resonance at room temperature and does not have discrete signals for the *rac* and *meso* isomers down to 0 °C.[15] Additionally, heating of a THF solution of chiral dicarbonyl **2** to 50 °C did not result in broadening of the ^{31}P NMR signals, which clearly indicates a significantly higher barrier to isomerization of the *rac* and *meso* isomers in the Ti(II) complex. The mechanism of isomerization in the M(IV) complexes is depicted in Scheme 1. Ring slippage, inversion, and ring slippage change the absolute configuration of the chiral plane.[15] These structures resemble known metallocene phosphido complexes[18] and the recently reported examples of η^1 pyrrolyl complexes.[19] Metal oxidation state and d-electron count appear to play an important role in the isomerization of phosphatitanocenes.



(2)

Scheme 1. Mechanism for the Isomerization of Heterocyclopentadienyl Complexes[a]



[a] See ref 15.

An explanation for the difference between the rates of isomerization in different oxidation states depends on the d-orbital in which the d-electrons are found for the Ti(II) complex (Figures 2 and 3). Employing the C_{2v} Cp_2ML_2 orbitals as a first-order model for the phospholyl analogue, it is possible to picture the interactions of importance in the ground state and at the transition state for the isomerization. The a_1-orbital pictured in Figure 2c is the LUMO of the d^0 complex (Figure 2a), and it is the HOMO of a d^2 complex (Figure 2b).[20] In the ground state of a Ti(II) complex there is a bonding interaction between the filled metal a_1-like orbital and a π^*-orbital of the phospholyl ligand, as depicted in Figure 3a for $(C_4H_4P)_2Ti(CO)_2$. This interaction results in additional ground state stabilization of the chiral Ti(II) complex relative to the Ti(IV) analogue. The additional bonding interaction contributes to the decreased M−Ctr distance in the Ti(II) molecules (vide supra). A shorter M−Ctr distance in the low-valent state is also observed when comparing Zr(II) and Zr(IV) analogues, $(\eta^5\text{-}C_4Me_4P)_2ZrCl_2$, Zr−Ctr(av) = 2.284 Å[21] and $(\eta^5\text{-}C_4Me_4P)_2Zr(CO)_2$, Zr−Ctr(av) = 2.201 Å.[9]

But, additional ground state stabilization of the Ti(II) complex is not the only contributor to the con-

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[14] Hollis, T. K.; Wang, L. S.; Tham, F. *J. Am. Chem. Soc.* **2000**, *122*, 11737−11738.

[15] Hollis, T. K.; Ahn, Y. J.; Tham, F. S. *Chem. Commun.* **2002**, 2996−2997.

[16] For the first report of an intramolecular isomerization of a phospinoferrocene see: Curnow, O. J.; Fern, G. M. *Organometallics* **2002**, *21*, 2827−2829.

[17] At present we propose that multiple conformations of the *rac*/*meso* isomers are being observed consistent with the report for $(indenyl)_2Ti(CO)_2$. See: ref 6c, p 347. Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *93*, 199−204. Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E.; Samuel, E. *J. Organomet. Chem.* **1987**, *327*, 39−54.

[18] Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049−51. Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661−1717. For a recent reference see: Urnezius, E.; Klippenstein, S. J.; Protasiewicz, J. D. *Inorg. Chim. Acta* **2000**, *297*, 181−190.

[19] Tanski, J. M.; Parkin, G. *Organometallics* **2002**, *21*, 587−589.

[20] Adapted from: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 394−396. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−42. Green, J. C. *Chem. Soc. Rev.* **1998**, *27*, 263−271.

[21] Mathey, F.; Ricard, L. *Organometallics* **1988**, *7*, 921−926.

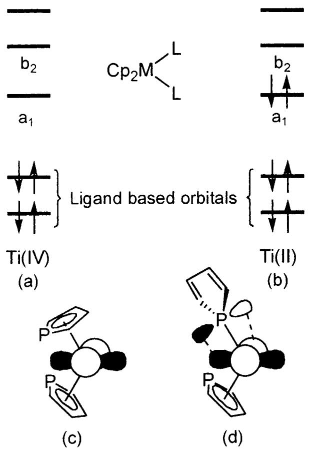

Figure 2. Frontier molecular orbitals for a C_{2v} Cp_2ML_2 fragment as a model for phospholyl analogues. (a) Orbital occupation for Ti(IV). (b) Orbital occupation for Ti(II). (c) The metal-centered symmetry adapted combination for the a_1-orbital is pictured in the ML_2 plane with L_2 omitted for clarity. (d) The P-lone pair in a p-orbital interacting with the a_1-orbital at the planar transition state of the inversion with L_2 omitted for clarity.

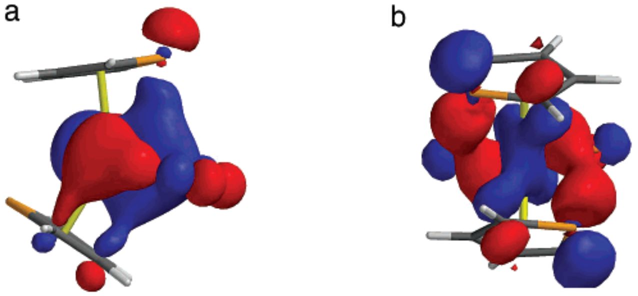

Figure 3. Orbital depictions of phosphatitanocenes (P is orange) with simplified models for the phospholyl ligands calculated with PCSpartan at the RHF/3-21G* level of (a) the HOMO of $(C_4H_4P)_2Ti(CO)_2$ (side view) with the crystal structure conformation, and (b) the geometry optimized LUMO of $(C_4H_4P)_2TiCl_2$ (viewed from behind the narrow side of metallocene wedge).

figurational stability of the chiral Ti(II) complexes. The a_1-like orbital is the LUMO of the Ti(IV) complex (Figures 2a,c and 3b). In the transition state for inversion the Ti atom is coplanar with the phospholyl ring and there will be overlap between the metal d-orbital and the p-π-orbital of P (Figure 2d). In the Ti(IV) complex the a_1-orbital is unoccupied (Figure 2a), and a two-electron−two-orbital stabilizing interaction occurs, which lowers the energy of the transition state for inversion. In contrast, in the Ti(II) complex the bonding a_1-orbital is occupied. Therefore, to undergo inversion the energy of the additional bonding interaction must be overcome. The major contributor to configurational stability is the interaction between the filled P-lone pair and the filled a_1-orbital at the transition state that results in a four-electron−two-orbital destabilizing interaction, which increases the activation barrier for inversion. Thus for the Ti(II) complex additional ground state stabilization and transition state destabilization both contribute to the increased configurational stability. This first-order explanation illustrates the importance of metal d-orbital occupancy in isomerization of heterocyclopentadienyl and other heterocyclic π-ligands.

To generalize, heterocyclic π-ligands that have a filled nonbonding orbital (e.g., a lone pair as in the phosphametallocenes) will have a stabilizing interaction with a vacant metal orbital in the planar transition state that lowers the barrier to isomerization. A d^0 metal is not necessarily required. In contrast, if the metal orbital that interacts with the lone pair is occupied, a destabilizing interaction occurs that results in a higher barrier to isomerization. These complexes should not isomerize as easily. The Ti(II) results reported here and previous observations are consistent with this conclusion. These occupancy rules are reversed for heterocyclic π-ligands with vacant nonbonding orbitals. For such complexes isomerization is predicted to be more facile if the metal has filled orbitals that can interact with the vacant orbital of the ligand, producing a two-electron−two-orbital stabilization at the transition state. Therefore, d^0 complexes are predicted to have higher barriers to isomerization, whereas metals with high d-orbital occupancy may have lower barriers to isomerization. But, a low barrier to isomerization is not guaranteed. An orbital of the proper symmetry, energy, and orientation must be available to interact with the vacant ligand orbital.

In summary, we report the first examples of low-valent phosphatitanocenes and the much slower rates of isomerization of a chiral Ti(II) d^2 complex versus its Ti(IV) d^0 counterpart. An explanation for the difference in isomerization rate has been advanced. Additional work is underway to determine the structures of the chiral Ti(II) complexes and to explore the Ti(II) phosphametallocene reactivity.

Experimental Section[22]

Bis(η^5-2,3,4,5-tetramethylphospholyl)titanium dicarbonyl, 1. 2,3,4,5-Tetramethyl-1-trimethylstannyl phosphole (1.16 g, 3.83 mmol)[5] and pentane (10 mL) were rapidly added to a solution of $TiCl_4 \cdot 2THF$ (0.59 g, 1.76 mmol) and CH_2Cl_2 (20 mL). After stirring 30 min, all volatiles were removed. The dark brown oil was extracted with pentane (40 mL). The extract was concentrated, and THF (15 mL) and Mg powder (86 mg, 3.54 mmol) were added. CO was bubbled through the dark green solution for 5 min and stirred overnight at 40 °C. The reaction was concentrated, and the resulting dark violet residue was extracted with pentane (50 mL). The extract was concentrated, yielding a red powder (270 mg, 39%). X-ray quality crystals were grown from a saturated toluene solution at −35 °C. ^1H NMR (C_6D_6, 300.053 MHz): δ 1.81 (s, 12H, β-CH_3), 1.59 (d, $^3J_{PH}$ = 9.75 Hz, 12H, α-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.475 MHz): δ 248. 4(Ti*C*O), 123.0 (d, $^2J_{PC}$ = 4.9 Hz, β-*C*), 117.3 (d, $^1J_{PC}$ = 52.5 Hz, α-*C*), 15.5 (d, $^2J_{PC}$ = 23.2 Hz, α-*C*H_3) 15.3 (m, β-*C*H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.474 MHz): δ 28.1 (s). IR (hexane, solution): 1959 (CO), 1900 (CO) cm^{-1}; (hexane, cast film) 1953 (CO), 1889 (CO) cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_2P_2Ti$: C, 56.57; H, 6.33; P, 16.21. Found: C, 56.45; H, 6.28; P, 15.96.

Bis(3,4-dimethyl-2-phenylphospholyl)titanium dicarbonyl, 2, was prepared in analogy with **1** from the isolated dichloride precursor.[15] A brown powder was obtained (75 mg, 35%). Isomer 1: ^1H NMR (C_6D_6, 300.053 MHz): δ 7.50−6.94 (m, 10H, C_6H_5), 4.76 (d, $^2J_{PH}$ =38.0 Hz, 2H, PC*H*), 1.98 (s, 6H, CH_3), 1.58 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.475 MHz): δ 245.7 (m, Ti*C*O). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.474 MHz): δ −13.63 (s). Isomer 2: ^1H NMR (C_6D_6, 300.053 MHz): δ 7.50−6.94 (m,

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[22] For general experimental details see ref 14. Elemental analyses were performed by Desert Analytics.

10H, C_6H_5), 4.43 (d, $^2J_{PH} = 38.0$ Hz, 2H, PC*H*), 1.85 (s, 6H, C*H*$_3$), 1.61 (s, 6H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.475 MHz): δ 243.8 (m, Ti*C*O). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.13 (s). IR (Et_2O, cast film): 1971(CO), 1914(CO) cm^{-1}; (hexane) 1992, 1981, 1975, 1931, 1918(CO) cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_2P_2Ti$: C, 65.29; H, 5.06; P, 12.95. Found: C, 65.34; H, 5.35; P, 12.81.

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Supporting Information Available: Full details of the crystal structure determination including tables of structural data and refinement, atomic coordinates, bond distances, bond angles, torsion angles, and anisotropic displacement parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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