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Longer but Stronger Bonds: Structures of PF_3, $P(OEt)_3$, and PMe_3 Adducts of an Open Titanocene

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Abstract: Single crystal X-ray diffraction studies have been carried out on the PF_3, $P(OEt)_3$, and PMe_3 monoadducts of the open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl), and on the PF_3 adduct of the corresponding vanadium compound. The titanium (vanadium) PF_3 adduct crystallizes in the monoclinic space group $P2_1/m$ (No. 11) with $a = 8.130(2)$ $(8.051(2))$ Å, $b = 14.277(5)$ $(14.313(4))$ Å, $c = 7.426(2)$ $(7.323(1))$ Å, $\beta = 116.17(2)°$ $(115.90(2)°)$, and $V = 773.59$ (758.97) Å^3 for $Z = 2$. The compound $Ti(2,4\text{-}C_7H_{11})_2PMe_3$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 7.889(4)$ Å, $b = 15.312(7)$ Å, $c = 15.072(7)$ Å, $\beta = 101.81(4)°$, and $V = 1782.1$ Å^3 for $Z = 4$, while the $P(OEt)_3$ adduct crystallizes in the tetragonal space group $I\bar{4}$ (No. 82) with $a = b = 23.406(4)$ Å, $c = 8.406(2)$ Å, and $V = 4605.1$ Å^3 for $Z = 8$. The studies reveal $Ti{-}PX_3$ bond lengths of 2.550(2), 2.472(4), and 2.324(1) Å for X = Me, OEt, and F, respectively, and a $V{-}PF_3$ bond length of 2.246(1) Å. A comparison with previously reported $Ti{-}PX_3$ binding energies demonstrates that while the $Ti{-}PMe_3$ bond is longer than the $Ti{-}P(OEt)_3$ bond, it is nonetheless significantly stronger, and the $Ti{-}PX_3$ bond lengths in these species seem to be determined primarily by the electronegativity of the phosphine substituents X. It can be expected that such situations may be fairly common in other classes of compounds.

Chemical bonds are the heart of chemistry, and their relative strengths play a dominant role in determining the course of chemical transformations. It is therefore a matter of great importance that a sound understanding of the fundamental properties of these bonds be achieved. Perhaps one of the most universally accepted tenets in chemistry is that a shorter bond (of a given type[4]) reflects a stronger bond.[5] If not always explicitly stated, such assumptions are certainly implicit in most structural studies whenever bond distances are being compared.[6] Additionally, however, there are explicit formulas and correlations which relate bond shortening to bond strengthening, for both ionic[7] and covalent[8] species. Interestingly, there are situations for which bond lengths do not correlate with their expected *bond orders*, as in some multiply bound dimetallic compounds.[9] However, spectroscopic data for these species still suggest that the shorter bonds are the stronger ones. Herein we report structural studies on several phosphine and phosphite complexes of an open titanocene, $Ti(2,4\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl), which reveal that a longer Ti−P bond may indeed still be the stronger. Furthermore, the results suggest that such situations might not be uncommon, and could easily lead to confusion for a variety of metal and nonmetal compounds.

Experimental Section

The PF_3 and PMe_3 complexes of $Ti(2,4\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl) were prepared as previously described.[10] Single crystals of these compounds were prepared by slowly cooling concentrated solutions of these adducts in hydrocarbon solutions to ca. −20 °C. These were subsequently loaded into glass capillaries which were sealed under nitrogen atmospheres.

$Ti(2,4\text{-}C_7H_{11})_2P(OEt)_3$. To a solution of $Ti(2,4\text{-}C_7H_{11})_2$ in 25 mL of hexane under a nitrogen atmosphere was added a slight excess of $P(OEt)_3$. The solution changed from emerald green to an orange-yellow. The solution was concentrated to ca. 10 mL and cooled to −30

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Table 1. Summary of the Diffraction Studies for the $Ti(2,4\text{-}C_7H_{11})_2(PX_3)$ Complexes (X = CH_3 (I), OEt (II), F (III)) and $V(2,4\text{-}C_7H_{11})_2(PF_3)$ (IV)

	I	II	III	IV
formula	$TiC_{17}H_{31}P$	$TiC_{20}H_{37}O_3P$	$TiC_{14}H_{22}PF_3$	$VC_{14}H_{22}PF_3$
mol. wt.	314.3	404.4	326.2	329.2
space group	$P2_1/c$	$I\bar{4}$	$P2_1/m$	$P2_1/m$
lattice constants				
a (Å)	7.889(4)	23.406(4)	8.130(2)	8.051(2)
b (Å)	15.312(7)	23.406(4)	14.277(5)	14.313(4)
c (Å)	15.072(7)	8.406(2)	7.426(2)	7.323(1)
β (deg.)	101.81(4)	90	116.17(2)	115.90(2)
V (Å^3)	1782.10	4605.14	773.59	758.97
Z	4	8	2	2
d(calc) (g/cm^3)	1.17	1.17	1.40	1.44
λ	0.71073	0.71073	0.71073	0.71073
temp (°C)	18	18	18	18
cryst shape	needle	needle	bar	bar
size (mm)	0.25 × 0.25 × 0.91	0.32 × 0.38 × 0.9	0.58 × 0.34 × 0.22	0.3 × 0.45 × 0.7
linear abs coeff (cm^{-1})	5.50	4.48	6.64	7.52
scan type	$\theta-2\theta$	Ω	Ω	Ω
scan speed (deg/min)	2−4	2−4	1−12	1−12
abs treatment	ψ scan	ψ scan	DIFABS	DIFABS
trans. factor	0.90−1.00	0.91−1.00	0.95−1.07	0.87−1.12
scan range (deg)	2	1	1.25	1
2θ limits (deg)	3−60	2.5−60	2−60	2−60
min hkl	−12, 0, 0	0, 0, 0	0, 0, −10	0, 0, −11
max hkl	12, 22, 22	33, 33, 12	11, 20, 10	11, 21, 11
no. of unique obsd data	2821 (3σ)	1368 (2.5σ)	1463 (3σ)	1446 (3σ)
no. of variables	172	132	140	107
$R(F)$	0.071	0.071	0.042	0.054
$R_w(F)$	0.058	0.053	0.044	0.062
max diff Fourrier peak (e/Å^3)	0.13	0.46	0.59	0.45

Table 2. Comparison of the Bonding in the $M(2,4\text{-}C_7H_{11})_2(L)$ Complexes (Distances in Å, Angles in deg, and Energies in kcal/mol)

	ML =			
	$TiPMe_3$	$TiP(OEt)_3$	$TiPF_3$	VPF_3
M−P	2.550(2)	2.472(4)	2.324(1)	2.246(1)
$-\Delta H$ (Ti−P)[a]	14.5(8)	10.6(6)	17.4(8)	
P−X	1.818(4)	1.604(6)	1.545(3)	1.545(3)
M−C[1,5]	2.345(3)	2.333(5)	2.326(2)	2.283(2)
M−C[2,4]	2.346(2)	2.342(5)	2.328(1)	2.274(2)
M−C[3]	2.305(3)	2.324(7)	2.311(2)	2.258(3)
M−C(avg)	2.337	2.335	2.324	2.274
C−C(intl)	1.421(4)	1.412(8)	1.406(2)	1.408(3)
C−C(extl)	1.391(4)	1.404(7)	1.396(3)	1.410(3)
∠X−P−X(avg)	98.9	100.8	93.8	93.3
PX_3 cone angle	118[b]	134[a]	104[b]	104[b]
conformation angle[c]	3.0	1.7	0	0
tilt angle[d]	4.0	2.0	0.6	2.2
CH_3 tilt	2.0	2.7	3.3	1.7
∠C[1]−C[2]−C[3]	124.8(3)	124.9(5)	124.4(2)	123.9(3)
∠C[2]−C[3]−C[4]	130.7(5)	128.8(7)	129.7(2)	128.6(3)

[a] See refs 10a and 40b. The value of ΔH for the PF_3 adduct was determined by a competition with PMe_3, the difference in binding being 2.9 ± 0.2 kcal/mol. [b] See ref 17. [c] This refers to the twist of the ligands from the syn-eclipsed conformation, as defined by the angle between the two Ti−C3−$^1/_2$[C(1) + C(5)] planes. [d] This is the angle between dienyl ligand planes.

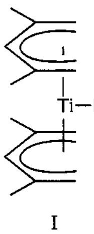
°C. The resulting red-orange crystals (mp 81−2 °C, dec) were isolated and dried under vacuum. This compound is thermochromic. Room temperature samples are orange-red but below ca. −30 °C the color of the monoadduct is yellow. A light green tinge is apparent when the sample is cooled in liquid nitrogen.

^{1}H NMR (toluene-d_8, −40 °C): δ 4.37 (s, 2H, H3), 3.93 (quintet, 6H, $P(OCH_2CH_3)_3$, J = 6.3 Hz), 2.68 (s, 4H, H_{exo}), 1.71 (s, 12H, CH_3), 1.18 (t, 9H, $P(OCH_2CH_3)_3$, J = 7.1 Hz), 1.03 (d of d, 4H, H_{endo}, J = 10.8, 4.8 Hz). ^{13}C NMR (toluene-d_8, −40 °C): δ 116.7 (s), 98.3 (d, J = 159 Hz), 59.7 (t, J = 144 Hz), 57.3 (t, J = 154 Hz), 30.3 (q, J = 126 Hz), 16.7 (q, CH_3, J = 126 Hz). IR (Nujol mull): 3080 (w), 1365 (sh), 1152 (w), 1095 (m), 1058 (sh), 1038 (sh), 1030 (s), 1000 (m), 938 (m), 925 (s), 862 (w), 840 (sh), 832 (m), 742 (sh), 730 (m), 720 (sh), 700 (sh) cm^{-1}. Anal. Calcd for $C_{20}H_{37}O_3PTi$: C, 59.40; H, 9.22. Found: C, 59.18; H, 9.38.

X-ray diffraction data for the PMe_3, $P(OEt)_3$, and PF_3 adducts were collected on Nicolet R3, Siemens-Stoe AED-II, and Nicolet $P\bar{1}$ diffractometers, respectively. Pertinent data collection parameters and structural quality indicators are presented in Table 1. An initial solution for the PMe_3 adduct was obtained by direct methods, while for the other three compounds the metal atom positions were obtained from Patterson maps. Subsequently the remaining non-hydrogen atoms were located by difference Fourier maps and least-squares refinements. For the $P(OEt)_3$ adduct, sufficient data to warrant full anisotropic refinement of the non-hydrogen atoms were not obtained due to its poorly diffracting nature, and hence the carbon atoms were refined isotropically. For the other structures, all non-hydrogen atoms could be refined anisotropically. Hydrogen atoms were placed in either positions suggested by difference Fourier maps or idealized locations, but they were not refined, except for the $Ti(2,4\text{-}C_7H_{11})_2PF_3$ structure. In the refinements the function minimized was $\Sigma w(|F_o| - |F_c|)$, for which $w = 1/\sigma^2(F)$ for the PMe_3 and $P(OEt)_3$ adducts, while for the PF_3 adducts, "ignorance factors" of 0.04 and 0.06, respectively, were employed.

Results

Important bond distances and bond angles are presented in Tables 2−6. Hydrogen atom parameters, atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, and least-squares planes information are contained in the supplementary material. The structures of the $Ti(2,4\text{-}C_7H_{11})_2(L)$ (C_7H_{11} = dimethylpentadienyl; L = PMe_3, $P(OEt)_3$, PF_3) and $V(2,4\text{-}C_7H_{11})_2(PF_3)$ complexes are illustrated in Figures 1−4. All four compounds have been found to adopt syn-eclipsed conformations, with the additional Lewis base situated by the open edges of the two dienyl ligands, as in **I**. Such arrangements



I

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Ti(2,4\text{-}C_7H_{11})_2[P(CH_3)_3]$

Bond Distances

Ti−C(1)	2.340(5)	Ti−C(8)	2.351(5)	C(1)−C(2)	1.365(7)	C(8)−C(9)	1.392(7)
Ti−C(2)	2.338(4)	Ti−C(9)	2.341(5)	C(2)−C(3)	1.433(7)	C(9)−C(10)	1.414(8)
Ti−C(3)	2.304(4)	Ti−C(10)	2.307(5)	C(3)−C(4)	1.417(8)	C(10)−C(11)	1.420(8)
Ti−C(4)	2.343(4)	Ti−C(11)	2.364(5)	C(4)−C(5)	1.403(7)	C(11)−C(12)	1.405(7)
Ti−C(5)	2.337(5)	Ti−C(12)	2.353(5)	C(2)−C(6)	1.513(8)	C(9)−C(13)	1.506(8)
Ti−P	2.550(2)	P−C(15)	1.790(5)	C(4)−C(7)	1.510(7)	C(11)−C(14)	1.500(7)
		P−C(17)	1.820(7)	P−C(16)	1.843(9)		

Bond Angles

C(1)−C(2)−C(3)	125.1(6)	C(8)−C(9)−C(10)	124.4(6)	Ti−P−C(15)	120.6(3)
C(1)−C(2)−C(6)	117.4(6)	C(8)−C(9)−C(13)	117.4(6)	Ti−P−C(16)	115.7(3)
C(2)−C(3)−C(4)	130.1(7)	C(9)−C(10)−C(11)	131.3(8)	Ti−P−C(17)	119.8(3)
C(3)−C(2)−C(6)	117.4(6)	C(10)−C(9)−C(13)	118.3(6)	C(15)−P−C(16)	99.2(5)
C(3)−C(4)−C(5)	125.0(6)	C(10)−C(11)−C(12)	124.5(6)	C(15)−P−C(17)	97.2(4)
C(3)−C(4)−C(7)	116.9(6)	C(10)−C(11)−C(14)	117.7(6)	C(16)−P−C(17)	100.2(7)
C(5)−C(4)−C(7)	118.1(5)	C(12)−C(11)−C(14)	117.6(5)		

Table 4. Bond Distances (Å) and Bond Angles (deg) for $Ti(2,4\text{-}C_7H_{11})_2P(OEt)_3$

Bond Distances

Ti−C(1)	2.328(10)	Ti−C(8)	2.333(9)	Ti−P	2.472(4)	C(9)−C(10)	1.385(16)
Ti−C(2)	2.327(11)	Ti−C(9)	2.344(11)	C(1)−C(2)	1.396(12)	C(9)−C(13)	1.497(16)
Ti−C(3)	2.323(11)	Ti−C(10)	2.324(9)	C(2)−C(3)	1.433(15)	C(10)−C(11)	1.426(16)
Ti−C(4)	2.340(11)	Ti−C(11)	2.358(10)	C(2)−C(6)	1.514(16)	C(11)−C(12)	1.424(14)
Ti−C(5)	2.331(10)	Ti−C(12)	2.341(11)	C(3)−C(4)	1.402(16)	C(11)−C(14)	1.496(14)
P−O(1)	1.628(10)	O(1)−C(15)	1.392(17)	C(4)−C(5)	1.385(14)	C(15)−C(16)	1.380(20)
P−O(2)	1.585(11)	O(2)−C(17)	1.450(18)	C(4)−C(7)	1.544(15)	C(17)−C(18)	1.412(22)
P−O(3)	1.598(8)	O(3)−C(19)	1.432(12)	C(8)−C(9)	1.410(14)	C(19)−C(20)	1.485(17)

Bond Angles

C(1)−C(2)−C(3)	124.6(10)	C(8)−C(9)−C(10)	125.2(10)	Ti−P−O(1)	114.2(4)
C(1)−C(2)−C(6)	119.8(10)	C(8)−C(9)−C(13)	117.1(10)	Ti−P−O(2)	123.1(4)
C(2)−C(3)−C(4)	127.6(10)	C(9)−C(10)−C(11)	130.0(9)	Ti−P−O(3)	114.0(3)
C(3)−C(2)−C(6)	115.5(8)	C(10)−C(9)−C(13)	117.7(9)	P−O(1)−C(15)	130.3(10)
C(3)−C(4)−C(5)	126.8(10)	C(10)−C(11)−C(12)	123.2(9)	P−O(2)−C(17)	114.2(8)
C(3)−C(4)−C(7)	114.7(9)	C(10)−C(11)−C(14)	116.7(9)	P−O(3)−C(19)	125.5(6)
C(5)−C(4)−C(7)	118.3(10)	C(12)−C(11)−C(14)	120.0(10)	O(1)−C(15)−C(16)	111.3(12)
O(1)−P−O(2)	93.7(5)	O(2)−P−O(3)	104.9(5)	O(2)−C(17)−C(18)	103.2(12)
O(1)−P−O(3)	103.8(5)			O(3)−C(19)−C(20)	106.4(9)

Table 5. Bond Distances (Å) and Angles (deg) for $Ti(2,4\text{-}C_7H_{11})_2PF_3$

Bond Distances

Ti−C(1)	2.338(3)	Ti−C(5)	2.314(3)	C(1)−C(2)	1.394(3)	C(5)−C(6)	1.398(4)
Ti−C(2)	2.326(2)	Ti−C(6)	2.331(2)	C(2)−C(3)	1.410(3)	C(6)−C(7)	1.403(3)
Ti−C(3)	2.305(3)	Ti−C(7)	2.317(3)	C(2)−C(4)	1.506(4)	C(6)−C(8)	1.519(4)
Ti−P	2.324(1)	P−F(1)	1.539(4)	P−F(2)	1.554(4)	P−F(3)	1.541(4)

Bond Angles

C(1)−C(2)−C(3)	124.2(2)	C(5)−C(6)−C(7)	124.6(3)	Ti−P−F(1)	124.2(2)
C(1)−C(2)−C(4)	118.7(2)	C(5)−C(6)−C(8)	118.6(3)	Ti−P−F(2)	123.4(2)
C(2)−C(3)−C(2')	129.7(3)	C(6)−C(7)−C(6')	129.6(4)	Ti−P−F(3)	119.7(2)
C(3)−C(2)−C(4)	117.1(2)	C(7)−C(6)−C(8)	116.8(3)	F(1)−P−F(2)	95.0(3)
F(1)−P−F(3)	91.1(3)			F(2)−P−F(3)	95.4(3)

Table 6. Selected Bond Distances (Å) and Angles (deg) for $V(2,4\text{-}C_7H_{11})_2PF_3$

Bond Distances

V−C(1)	2.289(3)	V−C(5)	2.277(3)	C(1)−C(2)	1.408(4)	C(5)−C(6)	1.412(5)
V−C(2)	2.274(3)	V−C(6)	2.275(3)	C(2)−C(3)	1.407(3)	C(6)−C(7)	1.409(4)
V−C(3)	2.248(4)	V−C(7)	2.269(4)	C(2)−C(4)	1.495(5)	C(6)−C(8)	1.500(5)
V−P	2.246(1)	P−F(1)	1.533(5)	P−F(2)	1.547(5)	P−F(3)	1.556(5)

Bond Angles

C(1)−C(2)−C(3)	123.2(3)	C(5)−C(6)−C(7)	124.6(4)	V−P−F(1)	124.5(2)
C(1)−C(2)−C(4)	118.7(3)	C(5)−C(6)−C(8)	118.5(4)	V−P−F(2)	124.6(2)
C(2)−C(3)−C(2')	129.3(4)	C(6)−C(7)−C(6')	127.8(5)	V−P−F(3)	119.3(2)
C(3)−C(2)−C(4)	118.0(3)	C(7)−C(6)−C(8)	116.8(4)	F(1)−P−F(2)	94.0(3)
F(1)−P−F(3)	89.9(4)			F(2)−P−F(3)	96.1(3)

had been expected for at least the titanium complexes, whose ^1H and ^{13}C NMR spectra had indicated highly symmetric structures.[10,11] The same could not be assumed with certainty for the paramagnetic vanadium analog, given that an alternative geometry involving η^5-*S*-dienyl (*S* = sickle) coordination (**II**) has been demonstrated structurally for relatives such as Cr-

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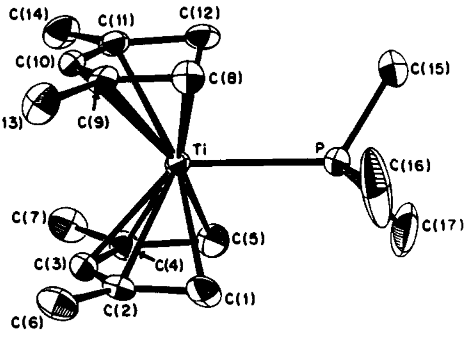


Figure 1. Molecular structure of $Ti(2,4\text{-}C_7H_{11})_2PMe_3$.

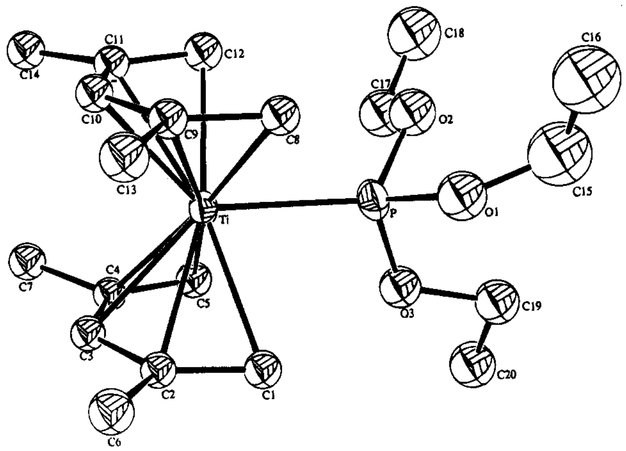


Figure 2. Molecular structure of $Ti(2,4\text{-}C_7H_{11})_2P(OEt)_3$.

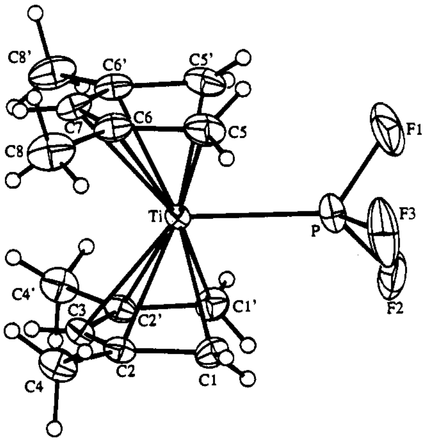
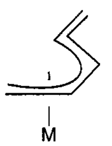


Figure 3. Molecular structure of $Ti(2,4\text{-}C_7H_{11})_2PF_3$. The molecule sits on a crystallographically imposed mirror plane of symmetry, rendering the PF_3 ligand disordered. One of the two PF_3 images is shown.



II

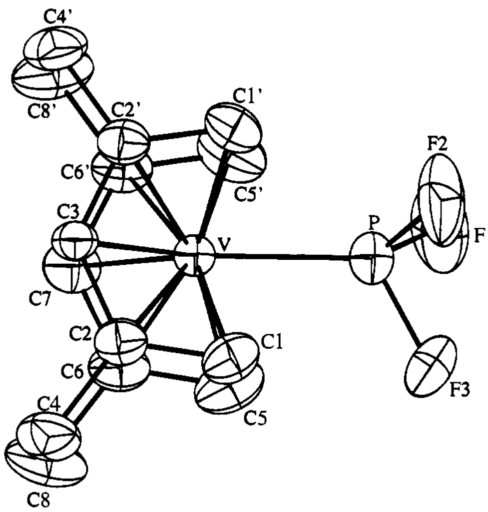
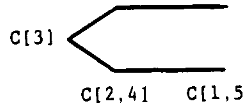


Figure 4. Molecular structure of $V(2,4\text{-}C_7H_{11})_2PF_3$. The PF_3 ligand is subject to the same disorder as in the titanium analog (Figure 3).

$(C_5H_5)(C_5H_7)$(2,6-xylylisocyanide)[12] and $M(2,4\text{-}C_7H_{11})_2PEt_3$ (M = Mo, W).[13,14] As can be seen from the small values of the conformation and tilt angles (Table 2), the deviations of the structures from the ideal syn-eclipsed geometry are essentially negligible, although a slight increase in these deviations might accompany an increase in the M−P distances. The orientations of the PX_3 ligands relative to the pentadienyl ligands are in accord with previous observations,[13,14] i.e., the PF_3 and PMe_3 adducts have one F or Me group lying midway between the two dienyl planes so that each of the other two F or Me groups points toward a terminal CH_2 group of a different dienyl ligand (see Figures 1, 3, and 4), while for the $P(OEt)_3$ structure, one OEt group is situated between the two CH_2 groups of a single dienyl ligand, resulting in the other two OEt groups pointing toward the two terminal CH_2 groups of the other dienyl ligand (see Figure 2).

The dienyl ligand parameters are generally consistent with the expected.[14] Thus, the external C−C bonds appear slightly shorter than the internal ones, due to a contribution from a resonance form having negative charge located on the central pentadienyl carbon atom, while the C−C−C angles about the methylated carbon atoms are smaller (by ca. 5°) than the angles about the central carbon atoms (Table 2). The methyl groups experience tilts from the dienyl plane of ca. 2−3° toward the metal, an apparent attempt to improve the overlap between metal and ligand orbitals.[15] In general, the magnitude of this tilt tends to be ca. 6−9°, and the smaller value in these cases may easily be attributed to the eclipsing orientations of the methyl groups.

Using the general carbon atom designations below, one can notice a tendency for the M−C[3] bonds to be shorter than the others. Whether this arises from steric or electronic considerations is unclear. A small but probably real correlation is seen between the Ti−P and Ti−C distances, such that shorter Ti−P distances accompany shorter Ti−C distances. This may reflect a slight contraction in metal atom size as a result of a loss in electron density to the better accepting phosphine ligands, and it is consistent with conclusions reached on related bis(cyclopentadienyl)titanium complexes.[16]



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One can also observe an apparent correlation between the (revised[10a]) cone angles for the PX_3 ligands and the X−P−X angles in these structures. As the size of X increases from F to CH_3 to OEt, there seems to be a tendency for the X groups to spread out, which further increases the cone angle of the ligand. Interestingly, it had earlier been noted that the strength of the binding of the PX_3 ligands to the titanium centers correlated well with the steric demands of the PX_3 groups, although without structural data, account could not be taken of the differing Ti−P bond lengths. As cone angle estimations have assumed constant values of M−P bond lengths,[17] the fact that these lengths can vary widely indicates that these cone angles should not be a very precise measure of steric effects, particularly when phosphine ligands with very different electronic properties (and hence, M−P distances) are being compared. Thus, the good correlation observed between cone angle and PX_3 binding may have been better than it should have been, and perhaps an electronic effect favoring π-acid ligands offset the uncompensated steric repulsions that would be experienced by the π-acid ligands having the shorter M−P distances. It is interesting that theoretical studies suggest little difference in donor abilities of the various PX_3 ligands, but significantly greater π-accepting differences, favoring $PF_3 > P(OR)_3 > PR_3$.[18] Hence, in general it would appear more likely to find electronic effects favoring the accepting rather than the donating PX_3 ligands.[19]

The most interesting comparison, however, involves that between the M−P bond lengths and bond strengths. While the most strongly bound ligand, PF_3, does form the shortest bond (2.324(1) Å) to titanium, the data for PMe_3 and $P(OEt)_3$ are quite unusual. The Ti−PMe_3 bond is significantly stronger than the Ti−$P(OEt)_3$ bond,[10a] 14.5(8) vs 10.6(6) kcal/mol, but it is also significantly longer, 2.550(2) vs 2.472(4) Å. We have recently observed a similar bonding trend for $Ti(C_8H_{11})_2(L)$ complexes (C_8H_{11} = cyclooctadienyl).[20] Clearly the Ti−P bond lengths and bond strengths are not directly correlated (vide infra). The Ti−P lengths observed here are similar to ones found in $Ti(C_5H_5)_2(PF_3)_2$ (2.344(3) Å), $Ti(C_5H_5)_2(PMe_3)_2$ (2.526(2) Å), and $Ti(C_5H_5)_2(CO)(PMe_3)$ (2.544(1) Å).[16,21]

Several differences are apparent between the two $M(2,4\text{-}C_7H_{11})_2(PF_3)$ structures (M = Ti, V) and correlate well with the larger size of Ti(II) relative to V(II).[22] Thus, the Ti−C bonds are ca. 0.05 Å longer than the V−C bonds, while the Ti−P bond is nearly 0.08 Å longer than the V−P bond. Quite similar trends were observed for $M(2,4\text{-}C_7H_{11})_2(PEt_3)$ complexes (M = Zr, Nb, Mo).[13] The fact that the M−P bonds shorten more than the M−C bonds on going to the more electron rich metals might be a result of increased backbonding to the phosphine ligands.

Discussion

The concept that shortening of a bond must reflect strengthening appears nearly universal. To some degree, the great extent to which this has been assumed to apply to general situations has probably come about due to overly optimistic extrapolations from simpler systems, for which more thermochemical data were available. Of course, some of the earliest correlations in the simpler systems focussed on lattice structures, and correlations as well as explicit formulas have been provided which reflect the dependence of bond length on either bond order or on bond energy.[7a] As more data have become available, bond strength−bond length correlations have been developed for very specific classes of ionic compounds, e.g., metal oxides and metal fluorides.[7b−e] Quite naturally, such considerations have also been presumed to extend to molecular species,[7a] and good correlations have indeed been observed for various classes of bonds, recent examples including sulfur−nitrogen, boron−oxygen, boron−nitrogen, and even rhodium−rhodium bonds.[8] Unfortunately, bond energy data are not abundant for most systems of interest and, hence, it is quite common that assumptions are made that shorter bonds (of a given type) must be stronger ones. Essentially blanket statements have been made to this effect, and it is generally recognized that such an assumption provides the motivation for determining structures to greater precisions than required simply for establishing molecular connectivity.[23] Thus, when shorter bonds are observed, they are almost inevitably assumed to be stronger, and an explanation is generally sought for the extra bond strength.

It is notable, however, that it has been established that bond length does not always correlate with bond order. Several such demonstrations have been provided for multiply bound metal−metal complexes, such as those of technetium and rhenium.[9] However, the observed bond lengths were found to correlate with M−M stretching frequencies. More recently, it has been reported that some N−F and O−F bond lengths do not correlate with their appropriate stretching force constants, although the uncertainties in the structural parameters were somewhat large relative to the observed bond length differences, and theoretically estimated force constants were used, since the spectroscopic data did not yield clear-cut force constants.[24]

For the more specific compound type at hand, namely, metal−phosphine and −phosphite complexes, there are again many instances in which shorter M−P bond lengths have been considered to reflect strong bonding. A good number of times it has been mentioned that M−$P(OR)_3$,[25] M−PF_3,[16,21,26] or M−$P(CF_3)_xR_{3-x}$[27] distances are significantly shorter than M−PR_3 distances, or indeed that M−PF_3 distances are shorter than M−$P(OR)_3$ distances, which are shorter than M−PR_3 distances.[5b,28] Identical observations have been made for M−CX_3, M−C_2X_4, or M−C_5X_5 complexes in which X can be a halogen or H.[29] In these regards, our structural data are quite reasonable. Much discussion has been focussed on these trends,[28a] and several mechanisms have been proposed to

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account for the bond shortening, particularly for the PF_3 complexes. Perhaps the most common explanation has been that as electronegative substituents are added to the phosphorus center, it should be capable of serving as a π-backbonding ligand, leading to stronger bonds.[21,25a−d,27b] The additional bonding then leads to bond shortening. In fact, it is quite generally accepted that PF_3 can indeed serve as a strong π-accepting ligand, apparently utilizing σ^* P−F orbitals as acceptors.[30] Naturally such considerations would lead to the expectation that $M{-}P(OR)_3$ bonds would also be shorter than $M{-}PR_3$ bonds, as we and others do indeed observe. Here, however, it becomes clear that the bond strengthening through π-backbonding explanation will not work. Thus, while the $Ti{-}P(OEt)_3$ bond length is significantly shorter than the $Ti{-}PMe_3$ bond length, 2.472(4) vs 2.550(2) Å, the bond strengths follow the opposite trend, 10.6(6) vs 14.5(8) kcal/mol. It would be unreasonable to propose $Ti{-}P(OEt)_3$ shortening due to *additional* π-bonding when, in fact, the actual bond energies show that not only is there no such additional bonding but the bond in question is actually weakened significantly.[31] In all likelihood, then, the "additional π-bonding" mechanism is not a principal means by which $M{-}PX_3$ bonds in general become shortened.

A second explanation for the shortening has been that since P−F (and P−O) bonds would have their electron density localized on F (or O), there would be correspondingly more s orbital density available for the phosphorus lone pair orbital.[28a,29a,32] In this regard it has often been assumed that changes in hybridization at the phosphorus centers would be reflected by the X−P−X angles.[25a,d,32−34] In fact, the X−P−X bond angles for the present examples (Table 2) do not show any particular trend with X electronegativity; rather, they seem to correlate with the steric demands of the PX_3 ligands themselves. This would seem to indicate that there was little change in the makeup of the phosphorus lone pair orbitals, and, indeed, similar observations have been made for other systems.[34] However, there are several indications that the situation may be more complex than it would appear. First, in at least some circumstances, hybrid orbitals may not be directed right at the atoms with which they interact.[35] In addition, the lone pair orbital in PH_3 seems to have a greater contribution from the phosphorus 3p orbital (characterized by a greater spatial extent than the 3s orbital[36]) than does the lone pair orbital of PF_3,[37] although these contributions would be subject to change upon coordination. It is therefore not clear to what extent, if any, hybridization changes contribute to the observed bond shortenings.

Finally, although not the most commonly cited explanation, the possible contraction of the phosphorus lone pair orbital as a result of electronegative substituents (F, OR) on the phosphorus center may be considered.[28b] This in fact would also seem capable of bringing about substantial effects, and it provides another possible explanation for the observed trend in M−P bond distance ($M{-}PF_3 < M{-}P(OR)_3 < M{-}PR_3$), since it allows for bond shortening to be observed without the necessity of invoking additional bonding interactions, and such an effect should be (and is) seen for both early and late transition metals, as well as nonmetals.[28a,b,38,39]

On the other hand, it could be proposed that the experimental Ti−P bond energies do not take into account P−X bond weakening that occurs as a result of π backbonding. In such a case, the true Ti−P bond energy would actually be greater than that measured, especially for PF_3 and the phosphite ligands, for which backbonding could be expected to be significant. However, the P−X bond weakening can be expected to be essentially a second-order effect, and should not be able to reverse the order between the $Ti{-}PMe_3$ and $Ti{-}P(OEt)_3$ bond energies, for which a rather large difference is observed, 14.5(8) vs 10.6(6) kcal/mol. Furthermore, one can find essentially no lengthening of the P−O bond lengths in $Ti(2,4\text{-}C_7H_{11})_2[P(OCH_2)_3CC_2H_5]$ as compared to those in a free cage phosphite, $P(OCH_2)_3CCH_2Br$ (1.614(3) vs 1.615(3) Å, respectively), indicating again that any P−O bond weakening should be very small.[40] A similar observation can be made for free[41] and bound PF_3 (1.570(1) vs 1.545(3) Å), although thermal libration may lead to a systematic shortening of the P−F bond lengths in $Ti(2,4\text{-}C_7H_{11})_2PF_3$. Similar observations have, however, been made for $M(CO)_5(PX_3)$ complexes (M = Cr, Mo, W),[30e] even from electron diffraction studies.[42] Actually, given that $M \rightarrow PX_3$ backbonding interactions are presumed now to involve σ^* P−X orbitals,[30] the lack of P−X bond lengthening upon coordination would appear contradictory to these claims. However, the PX_3 lone pair orbitals, prior to coordination, may contain appreciable σ^* P−X character,[37a,b] which would be reduced upon coordination, thereby providing an opposing (shortening) effect on the P−X bond lengths.

The results presented herein help to provide some clarification

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concerning the question of the origin of $M-PX_3$ bond shortening for the π-accepting phosphine ligands and furthermore provide a clear caveat for the numerous situations in which bond lengths are being or have been used as an indicator of bond strength. However, at the same time, the observed violation of the expected bond length–bond strength relationship occurs in a very recognizable situation, one in which significant differences in the electronegativities of attached atoms may be expected to lead to different orbital contributions or extensions. This is in fact parallel to the observed contraction of metal ion size as the oxidation state is increased.[22] Hence, it should not be difficult in related specific cases to realize that caution may be required. Further, in cases like $Pt(\eta^4\text{-}C_7H_8)(CH_3)(CF_3)$,[43] for which the $Pt-CH_3$ and $Pt-CF_3$ bond lengths are essentially the same (2.07(2) Å), it may provide reason to suppose that the $Pt-CH_3$ bond is stronger than the $Pt-CF_3$ bond. However, when such electronegativity complications do not exist, as generally is the case, it is quite likely that the usual bond length–bond strength expectations will hold.

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Supplementary Material Available: Tables of hydrogen atom parameters, positional and anisotropic thermal parameters for the non-hydrogen atoms, and least-squares plane data (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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