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Structure and Dynamics of a Seven-Coordinate Titanium Carbonyl Complex, Bis[1,2-bis(dimethylphosphino)ethane]tricarbonyltitanium†

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Bis[1,2-bis(dimethylphosphino)ethane]tricarbonyltitanium crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions of a = 16.068 (2) Å, b = 15.957 (3) Å, c = 8.627 (2) Å, and β = 96.10 (1)° at −100 °C. Full-matrix least-squares refinement of all coordinates and thermal parameters, using 2634 reflections, yielded R = 0.049 and R_w = 0.042. The compound is a seven-coordinate, monomeric, phosphine-substituted derivative of $Ti(CO)_7$. It ^{31}P stereochemically nonrigid. Variable-temperature ^{31}P and ^{13}C NMR measurements show two separable processes. The low-temperature process, $\Delta G^{\ddagger}$ = 7.77 kcal/mol, is consistent with rotation of a P–P–P triangular face; the high-temperature process, $\Delta G^{\ddagger}$ = 11.57 kcal/mol, equilibrates all phosphorus and carbonyl sites.

In our earlier studies of the chemistry of group 4B butadiene complexes, we found that high-pressure carbonylation of $Ti(\eta\text{-}C_4H_6)_2(dmpe)$[1] (dmpe = 1,2-bis(dimethylphosphino)ethane) or reductive carbonylation of $TiCl_4(dmpe)_2$ afforded a red, crystalline titanium carbonyl phosphine complex (**1**). This species had been reported as $[Ti(CO)_3(dmpe)_{3/2}]_n$ on the basis of analytical data. The compound was shown to react with PF_3 in the presence of excess dmpe to form $Ti(CO)_2(PF_3)(dmpe)_2$ (**2**), which was structurally characterized and shown to be a monomeric, phosphine-substituted derivative of the nonexistent $Ti(CO)_7$.[2] The well-known similarities of transition metal trifluorophosphine complexes and transition metal carbonyl complexes[3] suggested that **1** should have a similar stoichiometry to **2**. This led us to reexamine the formulation of **1**.

We have now succeeded in obtaining X-ray quality, single crystals of **1** and have structurally characterized the compound. The complex was, indeed, incorrectly formulated and is, in fact, $Ti(CO)_3(dmpe)_2$, the analogue of **2**. Seven-coordinate structures are commonly found for low-valent, early transition-metal derivatives, but very few are stereochemically rigid or exhibit dynamic behavior which is amenable to detailed analysis.[4] The complex **1** is stereochemically nonrigid, exchanging ^{31}P and ^{13}C sites, but can be quenched. The availability of structural details now allows us to interpret this phenomenon and propose a mechanism for exchange in this $Ti(CO)_7$ derivative.

Experimental Section

All operations were performed under an atmosphere of prepurified nitrogen or in vacuo. THF was distilled from sodium benzophenone ketyl. $Ti(CO)_3(dmpe)_2$ was prepared as described earlier.[2] NMR measurements were obtained with a Bruker HFX-90 spectrometer equipped with a Digilab FTS NMR-3 Data System. Low-temperature ^{31}P and ^{13}C data were obtained sequentially with the same probe/thermocouple assembly to minimize systematic temperature differences.

$Ti(^{13}CO)_3(dmpe)_2$. Approximately 50 mL of THF was condensed into a flask containing 0.619 g of $Ti(CO)_3(dmpe)_2$ (1.43 mmol) cooled to −196 °C. With the aid of a Töppler pump, 13.5 mmol of 90% enriched ^{13}CO was admitted to the flask. After being warmed to room temperature, the mixture was stirred for 4 h. The solution was then frozen, evacuated, treated with an additional 13.5 mmol of 90% ^{13}CO, and warmed. After a total of three exchanges, the solution was evaporated to dryness and the remaining red solid $Ti(^{13}CO)_3(dmpe)_2$ washed with hexane. Mass spectral analysis of the CO recovered after each exchange indicated statistical exchange had occurred in each case, implying a final enrichment of 89%.

Crystallographic Analysis of 1. The X-ray study was carried out by using a Syntex P3 diffractometer (graphite monochromator; Mo Kα radiation, λ = 0.71069 Å) with the crystal cooled to −100 °C. A preliminary examination showed the crystal to be monoclinic with space group $P2_1/n$. The unit cell dimensions were refined from the Bragg angles of 50 reflections: a = 16.068 (2) Å, b = 15.957 (3) Å, c = 8.627 (2) Å, β = 96.10 (1)°. The cell volume, 2199 Å^3, yields a calculated density of 1.305 g cm^{-3} for Z = 4.

Intensity data for 5055 reflections were collected by using the ω scan technique (4° > 2θ < 55°; scan width of 1.0°; background measurements at both ends of the scan; total background time equal to the scan time). The intensities of four standard reflections were monitored after every 200 reflections; only statistical fluctuations were noted. The intensity of one reflection was measured in 10° increments about the diffraction vector (crystal dimensions 0.29 × 0.08 mm perpendicular to the capillary axis × 0.40 mm parallel to the axis), and, as a result, empirical corrections for adsorption were applied; transmission factors varied from 0.896 to 1.000.

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[5] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[6a] anomalous dispersion corrections were by Cromer.[6b] In the least-squares refinement, the function minimized was $\sum w(|F_0| - |F_c|)^2$ with the weights, w, assigned as $1/\sigma^2(F_0)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[7]

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† Contribution No. 3019.

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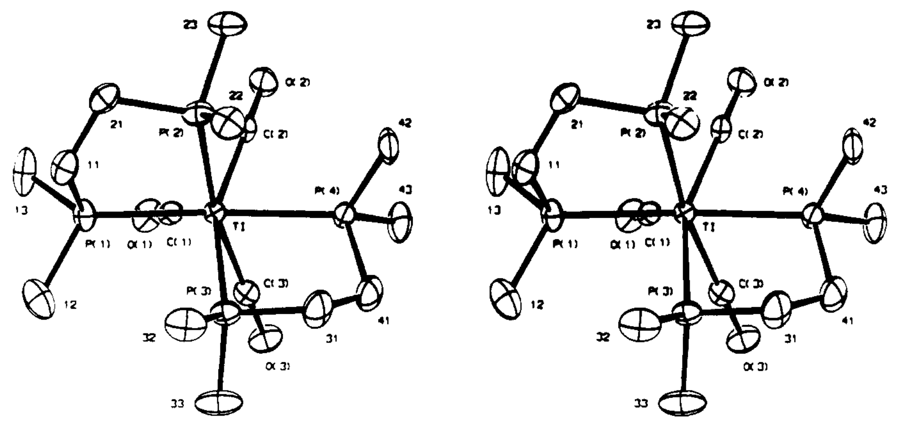


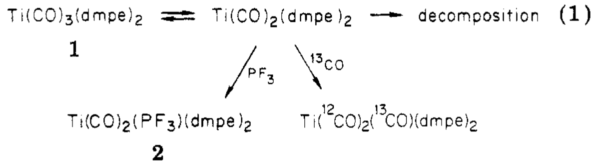
Figure 1. Stereodrawing of the molecule perpendicular to the P(1) → P(4) and P(2) → P(3) vectors.

The structure was refined by the full-matrix least-squares method. All of the non-hydrogen atoms in the structure were refined with anisotropic thermal parameters and the hydrogen atoms with isotropic parameters. A total of 336 parameters yielded $R = 0.049$ and $R_w = 0.042$ with GOF = 1.47 for 2634 reflections for which $F_o^2 > 3\sigma(F_o^2)$. The largest peak in the final difference Fourier map had a magnitude of 1.0 e Å^{-3} and was located 2.6 Å from Ti, 1.0 Å from P(2), and half-way between C(22) and C(23). It looked suspiciously like a phosphorus atom from a contaminant compound. The second and third largest peaks were 0.64 and 0.45 e Å^{-3} in magnitude, and these appeared to be unrelated to the first peak.

Results and Discussion

Although crystallizing readily from common organic solvents, single crystals of 1 were obtained only with difficulty and after repeated trials. Low-temperature crystallization from hexamethyldisiloxane afforded material adequate for X-ray analysis. The indicated composition of 1, $Ti(CO)_3(dmpe)_2$ (vide infra), is not in close agreement with analytical data nor is the analogous $Ti(CO)_3(depe)_2$ (depe = 1,2-bis(diethylphosphino)ethane); in both cases Ti/P ratios of approximately 1/3 are found.[2] However, the structure and composition of 1 reported below is representative of the bulk material as no impurities are observed in the ^{31}P and ^{13}C NMR spectra or IR spectra. Indeed, the NMR data are less consistent with the earlier formulation. The inaccurate analytical results are likely a reflection of the thermal instability of 1 and presumably reflect decomposition occurring during transmittal to the analyst.

The compound is labile, rapidly exchanging carbonyls with PF_3, as previously described,[2] or with ^{13}CO at room temperature. Indeed, 1 slowly decomposes at room temperature unless kept under a CO atmosphere. These properties suggest that 1 is capable of undergoing a reversible dissociation of CO, forming the 16-electron, octahedral complex $Ti(CO)_2(dmpe)_2$ (eq 1). No direct evidence is presently available to support this hypothesis, however.



$$\underset{1}{Ti(CO)_3(dmpe)_2} \rightleftharpoons Ti(CO)_2(dmpe)_2 \longrightarrow \text{decomposition} \quad (1)$$

$$Ti(CO)_2(dmpe)_2 \xrightarrow{PF_3} \underset{2}{Ti(CO)_2(PF_3)(dmpe)_2} \qquad Ti(CO)_2(dmpe)_2 \xrightarrow{^{13}CO} Ti(^{12}CO)_2(^{13}CO)(dmpe)_2$$

Structural Results. The structure of 1 in Figure 1 may be regarded as a monocapped octahedron–P(1) and P(4) defining the apices, P(2), P(3), C(3), and C(2) representing equatorial sites, and the C(1) carbonyl group capping the C(3)–C(2)–P(1) octahedral face. At best, this is an approximate description as substantial deviations from the idealized geometry are present. For example, the P(4)–Ti–P(1) angle is ca. 160° rather than the expected 180°, and the C(2)–Ti–C(3) angle is 102° rather than the expected 90°. Moreover, the equatorial plane is poorly defined with each of the four atoms deviating from the least-squares plane by more than 0.1 Å; the Ti is displaced 0.35 Å from this plane toward P(4). Removal of the capping carbonyl group, defined by C(1), gives an *approximately* octahedral C_2 structure. The structure of $Ti(CO)_2(PF_3)(dmpe)_2$ is not closely related; it better approximates a monocapped trigonal prism but can be described in terms of a monocapped octahedron. Formally, the $Ti(CO)_2(PF_3)(dmpe)_2$ structure can be derived from that of 1 by replacing the C(2) carbonyl group with a PF_3 ligand and repositioning the capping carbonyl group C(1) on the P(2)–C(2)–P(4) octahedral face.

Table I. Selected Bond Distances (Å) and Bond Angles (Deg)

A. Bond Distances

Ti-P(1)	2.567 (1)	P(2)-C(23)	1.826 (5)
Ti-P(2)	2.637 (1)	P(3)-C(31)	1.874 (6)
Ti-P(3)	2.630 (1)	P(3)-C(32)	1.817 (5)
Ti-P(4)	2.523 (1)	P(3)-C(33)	1.808 (6)
Ti-C(1)	1.970 (4)	P(4)-C(41)	1.830 (5)
Ti-C(2)	1.997 (4)	P(4)-C(42)	1.826 (6)
Ti-C(3)	1.990 (4)	P(4)-C(43)	1.815 (5)
P(1)-C(11)	1.841 (5)	C(1)-O(1)	1.187 (4)
P(1)-C(12)	1.827 (6)	C(2)-O(2)	1.174 (5)
P(1)-C(13)	1.819 (6)	C(3)-O(3)	1.181 (4)
P(2)-C(21)	1.853 (5)	C(11)-C(21)	1.525 (7)
P(2)-C(22)	1.833 (5)	C(31)-C(41)	1.517 (7)

B. Bond Angles

P(1)-Ti-P(2)	75.34 (4)	P(3)-Ti-C(1)	130.5 (1)
P(1)-Ti-P(3)	85.08 (4)	P(3)-Ti-C(2)	155.7 (1)
P(1)-Ti-P(4)	159.51 (4)	P(3)-Ti-C(3)	79.4 (1)
P(1)-Ti-C(1)	77.3 (1)	P(4)-Ti-C(1)	123.0 (1)
P(1)-Ti-C(2)	115.5 (1)	P(4)-Ti-C(2)	77.7 (1)
P(1)-Ti-C(3)	114.1 (1)	P(4)-Ti-C(3)	75.9 (1)
P(2)-Ti-P(3)	92.51 (4)	C(1)-Ti-C(2)	69.7 (2)
P(2)-Ti-P(4)	92.22 (4)	C(1)-Ti-C(3)	67.1 (2)
P(2)-Ti-C(1)	125.7 (1)	C(2)-Ti-C(3)	101.7 (2)
P(2)-Ti-C(2)	81.3 (1)	Ti-C(1)-O(1)	176.3 (3)
P(2)-Ti-C(3)	166.6 (1)	Ti-C(2)-O(2)	176.7 (4)
P(3)-Ti-P(4)	79.19 (4)	Ti-C(3)-O(3)	177.2 (3)

The Ti–P distances in 1 are, as expected, shorter for the trans phosphorus atoms (2.567 and 2.523 Å) than for cis pair (2.637 and 2.630 Å).[8] These distances are within the range found in $Ti(CO)_2(PF_3)(dmpe)_2$, 2.509–2.671 Å.[2]

Dynamics of 1. The $^{31}P\{^1H\}$ spectrum of 1 obtained in THF/toluene-d_8 solvent is unaffected by viscosity down

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[8] Compare *cis*-$Cr(CO)_2(PH_3)_4$: Huttner, G.; Schelle, S. *J. Cryst. Mol. Struct.* **1971**, *1*, 69.

Table II. Atomic Coordinates for $Ti(CO)_3(dmpe)_2$

atom	x	y	z	atom	x	y	z
Ti	0.50453 (5)	0.23721 (5)	0.12883 (9)	C(11)	0.3974 (3)	0.1234 (3)	0.4209 (5)
P(1)	0.42744 (8)	0.10901 (8)	0.2226 (1)	C(12)	0.4764 (4)	0.0055 (4)	0.2322 (7)
P(2)	0.43486 (8)	0.29102 (9)	0.3737 (1)	C(13)	0.3266 (4)	0.0816 (4)	0.1188 (6)
P(3)	0.63547 (8)	0.17730 (9)	0.3026 (1)	C(21)	0.3615 (3)	0.2112 (4)	0.4358 (6)
P(4)	0.60219 (8)	0.36133 (8)	0.1367 (1)	C(22)	0.4945 (3)	0.3135 (4)	0.5622 (6)
O(1)	0.4113 (2)	0.1700 (2)	−0.1871 (3)	C(23)	0.3661 (3)	0.3824 (4)	0.3530 (6)
O(2)	0.3885 (2)	0.3768 (2)	−0.0433 (4)	C(31)	0.7059 (3)	0.2693 (4)	0.3511 (7)
O(3)	0.6224 (2)	0.1978 (2)	−0.1343 (3)	C(32)	0.6472 (4)	0.1305 (4)	0.4957 (6)
C(1)	0.4442 (3)	0.1941 (3)	−0.0656 (5)	C(33)	0.7018 (3)	0.1073 (4)	0.2061 (6)
C(2)	0.4315 (3)	0.3265 (3)	0.0247 (5)	C(41)	0.7078 (3)	0.3302 (4)	0.2165 (7)
C(3)	0.5801 (3)	0.2116 (3)	−0.0334 (5)	C(42)	0.5861 (3)	0.4524 (3)	0.2582 (6)
				C(43)	0.6214 (4)	0.4095 (4)	−0.0468 (6)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(11)A	0.355 (3)	0.084 (3)	0.440 (5)	3.1 (11)	H(31)A	0.680 (4)	0.305 (5)	0.448 (8)	12.4 (25)
H(11)B	0.446 (3)	0.109 (3)	0.483 (5)	4.1 (12)	H(31)B	0.771 (3)	0.243 (4)	0.380 (6)	5.8 (14)
H(12)A	0.524 (3)	0.014 (3)	0.309 (6)	6.5 (16)	H(32)A	0.609 (4)	0.082 (5)	0.467 (8)	11.1 (23)
H(12)B	0.439 (3)	−0.045 (3)	0.268 (5)	4.0 (12)	H(32)B	0.702 (3)	0.125 (3)	0.534 (5)	4.2 (12)
H(12)C	0.487 (3)	−0.016 (3)	0.123 (5)	4.8 (13)	H(32)C	0.629 (3)	0.171 (4)	0.571 (6)	6.0 (15)
H(13)A	0.288 (3)	0.125 (3)	0.122 (5)	4.3 (13)	H(33)A	0.708 (4)	0.127 (4)	0.119 (7)	8.2 (19)
H(13)B	0.335 (3)	0.064 (3)	0.017 (5)	4.4 (12)	H(33)B	0.754 (3)	0.098 (3)	0.272 (5)	2.3 (10)
H(13)C	0.302 (3)	0.034 (3)	0.173 (5)	4.1 (12)	H(33)C	0.668 (2)	0.057 (3)	0.195 (4)	1.9 (9)
H(21)A	0.354 (3)	0.228 (3)	0.550 (5)	2.6 (10)	H(41)A	0.732 (4)	0.283 (4)	0.147 (7)	9 (2)
H(21)B	0.307 (3)	0.217 (3)	0.359 (6)	6.2 (15)	H(41)B	0.740 (3)	0.382 (3)	0.232 (5)	2 (1)
H(22)A	0.530 (3)	0.356 (4)	0.549 (6)	6.7 (16)	H(42)A	0.537 (3)	0.469 (3)	0.224 (5)	3 (1)
H(22)B	0.459 (3)	0.329 (3)	0.640 (5)	3.2 (11)	H(42)B	0.566 (3)	0.432 (3)	0.375 (5)	4 (1)
H(22)C	0.518 (3)	0.256 (3)	0.605 (5)	4.4 (12)	H(42)C	0.619 (3)	0.491 (3)	0.244 (5)	4 (1)
H(23)A	0.396 (3)	0.432 (3)	0.326 (5)	4.2 (12)	H(43)A	0.568 (3)	0.428 (3)	−0.098 (5)	5 (1)
H(23)B	0.318 (3)	0.373 (3)	0.270 (6)	5.5 (14)	H(43)B	0.663 (3)	0.448 (3)	−0.037 (6)	5 (1)
H(23)C	0.337 (3)	0.396 (3)	0.447 (6)	5.3 (14)	H(43)C	0.640 (3)	0.372 (3)	−0.106 (5)	3 (1)

to −115 °C where four distinct, equally intense resonances are observed at 50.8, 32.6, 17.0, and 8.1 ppm downfield of H_3PO_4. Limiting slow exchange is not achieved because of solvent viscosity at lower temperatures, so detailed coupling information is not obtained. Four inequivalent ^{31}P sites are consistent with the C_1 ground-state structure.

At intermediate temperatures the inner pair of lines (32.6, 17.0 ppm) exchange while the outer lines remain sharp until at −60 °C and the spectrum has collapsed to three lines of relative intensity, 1:2:1. A simple noncoupled, two-site model was used to obtain the activation parameters (Table III).

At −40 °C additional exchange of all three sites begins, and at +40 °C the spectrum has reduced to one broad line, implying equivalence of both dmpe ligands. This process was fit by a model which allowed exchange between the two dmpe ligands as well as exchange of the ends of the formally static dmpe; that is, a concerted intramolecular process with total randomization. The latter motion was necessary to account for the reduced intensity of the outer lines.

The quenched $^{13}C\{^{31}P, ^1H\}$ spectrum (−113 °C) shows three inequivalent carbonyl sites at 300.7, 282.1, and 268.3 ppm downfield of Me_4Si. ^{13}C–^{13}C coupling is evident but is not sufficiently resolved to provide structural information.

Increasing temperature causes exchange of the two higher field lines while the downfield peak remains sharp. At −60 °C the spectrum has collapsed to two lines of intensity 1:2. A simple two-site model gives activation parameters (Table II) which are similar to those of the lower energy ^{31}P exchange, implying the same process is responsible. The $\Delta G^{\ddagger}$ values are almost identical, but the component $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ differ appreciably. We interpret this deviation as an inherent limitation to the line-shape fitting rather than being to two independent processes. We favor the data from the ^{31}P process, on the basis of sensitivity advantages and more accurate temperature control with the lower power decoupling used. Arrhenius plots for both ^{31}P and ^{13}C data are linear (Figure 2).

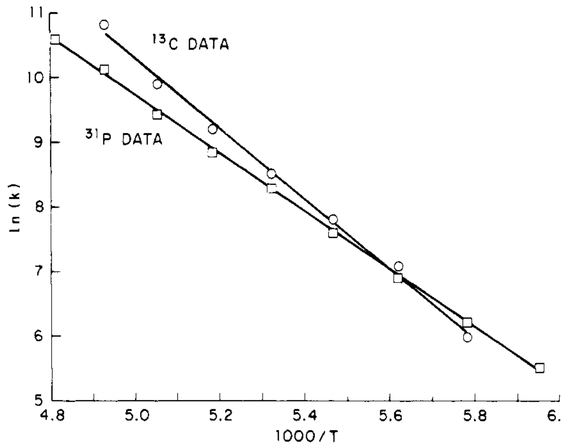

Figure 2. Arrhenius plots of ^{13}C and ^{31}P NMR derived rate data for the low-temperature process.

Table III. Activation Parameters[a,b] for ^{13}P and ^{13}C Exchange in $Ti(CO)_3(dmpe)_2$

	^{31}P NMR Data	^{13}C NMR Data
A. Low-Temperature Process		
$\Delta G^{\ddagger}$ (183 K)	7.77 (2)	7.71 (5)
$\Delta H^{\ddagger}$	8.6 (2)	10.4 (8)
$\Delta S^{\ddagger}$	4 (2)	14 (4)
B. High-Temperature Process		
$\Delta G^{\ddagger}$ (263 K)	11.57 (8)	11.34 (31)
$\Delta H^{\ddagger}$	11.3 (8)	9.5 (30)
$\Delta S^{\ddagger}$	−1 (2)	−7 (12)

[a] $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ in kcal/mol; $\Delta S^{\ddagger}$ in cal/(K mol). [b] Uncertainty limits refer to 95% confidence limits in the fit to the Eyring equation, assuming unit transmission coefficients.

Above −40 °C another exchange process equilibrates the unique carbonyl with the other two. Kinetic information is less satisfactory because of low sensitivity and because

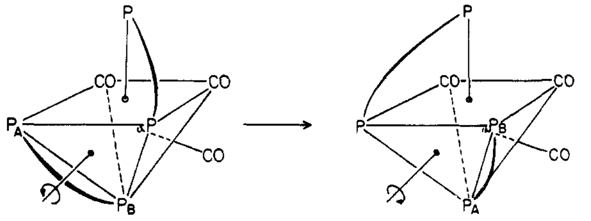

Figure 3. Proposed low-temperature process.

spectra were obtained at different times; however, the exchange parameters are again similar to those of the ^{31}P process (Table III).

We propose a mechanism for the low-temperature process involving a trigonal twist of either the P(4)-P(2)-P(3) or the P(1)-P(2)-P(3) face of 1. This concerted process simultaneously equilibrates two carbonyls and the ends of one dmpe ligand. Cyclic interchange P(4) → P(2) → P(3) produces the enantiomer of 1, where P(3)-P(4) and C(2)-C(3) have simultaneously equilibrated (Figure 3). Additionally, permutting P(2) → P(3) → P(1) exchanges P(1)-P(2) and C(2)-C(3). There is no physical basis for distinguishing between rotation of the upper or lower P-P-P face. Trigonal twists of the other six faces do not effect the required exchange. Other mechanisms may be possible, but the one described above represents the simplest conceivable intramolecular process. Dissociative arm on-arm off processes are unlikely as there is no uniquely long Ti-P bond.

We cannot distinguish between a large number of possible mechanisms for the high-temperature process.

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Registry No. 1, 81830-93-5; $Ti(^{13}CO)_3(dmpe)_2$, 81830-94-6.

Supplementary Material Available: A listing of all bond angles and distances (Table IV), atomic coordinates and thermal parameters (Table V), and structure amplitudes (Table VI) (24 pages). Ordering information is given on any current masthead page.

Electrochemical Generation of Stable Cations of (Arene)tricarbonylchromium Complexes. Studies on the Noninteraction of the Tricarbonylchromium Groups in Bis and Tris Complexes

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Complexes of the type $(CH_3)_2Sn[ArCr(CO)_3]_2$ were studied by cyclic voltammetry. The compounds can be made to undergo chemically reversible oxidation upon judicious choice of conditions and modification of Ar. The persistence of the cations seems to be a function of the steric bulk around the phenyl rings. Oxidation involves one electron per tricarbonylchromium group. The tricarbonylchromium moieties are essentially noninteracting and therefore adhere to the Bard-Anson-Saveant model. The same results are found for the bis and tris complexes of methyltriphenyltin where a dication and trication are formed, respectively. The structure of $(CH_3)_2Sn[2,4,6\text{-}(CH_3)_3C_6H_2Cr(CO)_3]_2$ was determined from 5287 observed diffractometer data and refined to an R value of 4.4%. The compound crystallizes in space group $P2_1/c$ with $Z = 4$ and lattice constants of $a = 15.514$ (2) Å, $b = 13.026$ (2) Å, $c = 15.709$ (2) Å, and $\beta = 119.51$ (1)°. The structure consists of a tin atom that is bonded to two methyl and two mesityl groups in a distorted tetrahedral geometry. Each mesityl group is also bonded to a $Cr(CO)_3$ moiety in a η^6 fashion. The average Sn-C(methyl) and Sn-C(mesityl) distances are 2.149 (4) and 2.182 (3) Å, respectively. When the Cr-CO bonds are projected onto the mesityl plane, they eclipse the methyl-substituted ring carbon atoms.

Introduction

A number of electrochemical studies have been carried out on various (arene)tricarbonylchromium complexes. Gubin has reported a one-electron reversible reduction of (acetophenone)tricarbonylchromium.[2,3] The EPR work of Ceccon[4,5] on radical anions of complexes such as (*tert*-butyl phenyl ketone)tricarbonylchromium has confirmed the speculation of Gubin that the lowest vacant orbital is primarily on the carbonyl portion of the organic ligand. In addition, work, by Dessey and co-workers,[6,7] had demonstrated a two-electron reduction of (benzene)tricarbonylchromium which was characterized as "ill-behaved". Reductive electrolysis resulted in a stable yellow

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