Cluster Chemistry

The First Trimetallic Pd/Tl/Co Carbonyl Cluster, Trigonal $[Pd_9\{\mu_3\text{-}TlCo(CO)_3L\}(\mu_2\text{-}CO)_6(\mu_3\text{-}CO)_3L_6]$: Ligand-Stabilization of the Trigonal-Bipyramidal $[TlCo(CO)_3L]$ Entity**

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Dedicated to Professor R. Bruce King
on the occasion of his 66th birthday

In the course of our exploration of reactivities of carbonyl/phosphine clusters of palladium with thallium(I) complexes,[1] we have isolated approximately 40% yield) and crystallographically and spectroscopically characterized a remarkable 11-metal-atom pseudo-C_{3v} cluster, $[Pd_9\{\mu_3\text{-}TlCo(CO)_3L\}(\mu_2\text{-}CO)_6(\mu_3\text{-}CO)_3L_6]$, ($L = PEt_3$) (**1**), from reactions of $[Pd_4(CO)_5L_4]$ (**2**) and/or $[Pd_{10}(CO)_{12}L_6]$ (**3**) with $[TlCo(CO)_4]$. Its unusual solid-state molecular geometry was ascertained from a low-temperature X-ray diffractometry study. Cluster **1** furnishes the first crystallographic example of a trigonal-bipyramidal $[TlCo(CO)_3L]$ entity of thallium(I) which in **1** is stabilized as a ligand by tripalladium coordination; otherwise it would be unstable. The only other isolated non-phosphite L derivative of $[TlCo(CO)_4]$ is $[TlCo(CO)_3PPh_3]$,[2a] but even this molecular thallium(I) product was found to readily disproportionate into thallium(III) $[Tl\{Co(CO)_3PPh_3\}_3]$ and thallium metal.[2] Spectroscopic measurements including a multinuclear NMR ($^{205,203}Tl$, ^{31}P, ^{13}C, ^{1}H) investigation coupled with solid-state/solution IR and UV/Vis spectra have provided considerable insight concerning the indicated dynamic behavior of the entire $[TlCo(CO)_3PEt_3]$ ligand of **1** in solution.

Thallium(I) tetracarbonylcobaltate was initially prepared in 1942[3a] and 30 years later reliably introduced in synthetic organometallic chemistry by Robinson and co-workers[3b,c] as "a convenient and versatile source of the tetracarbonylcobaltate anion." They also showed from an X-ray diffraction study that crystalline $[TlCo(CO)_4]$ possesses an ionic NaCl-like cubic structure with the shortest Tl···Co separations being 3.55(1) Å.[3c] To date, the role of this compound has not been extended markedly beyond its proposed use in reactions with organic and organometallic halides; these reactions predictably result in the generation of carbon–cobalt or metal–cobalt bonds, respectively, along with formation of thallium(I) halides arising from complete breakdown of ion-pair $Tl^+[Co(CO)_4]^-$ interactions.[4] Although $[TlCo(CO)_4]$ has fulfilled the same role as the widely used $[NaCo(CO)_4]$, it may have additional synthetic potential owing to the filled $Tl^I\,6s^2$ atomic orbital. To our knowledge, **1** is the first example where the donor ability of this so-called "inert" electron pair of Tl^I has been realized with simultaneous retention of the Tl–Co bond, in this case through its triply bridging coordination to a triangular Pd_3 face of the octahedral unit of the Pd_9 core (see below).

Both the composition and atomic arrangement of **1** in the solid state were unambiguously established from a low-temperature single-crystal CCD X-ray crystallographic analysis[5a,b] which revealed two closely resembling independent molecules of pseudo C_{3v} symmetry in the unit cell.[5c] The overall geometry of **1** can be described as a distorted Pd_6 octahedron with three $Pd(\mu_2\text{-}CO)_2L$ fragments that each edge-bridge one triangular Pd_3 face of the Pd_6 octahedron (Figure 1). Its salient structural feature is the additional attachment of a trigonal-bipyramidal $[\mu_3\text{-}TlCo(CO)_3L]$ ligand to one Pd_3 triangle. The principal pseudo threefold axis passes through the P, Co, and Tl atoms and the centers of two

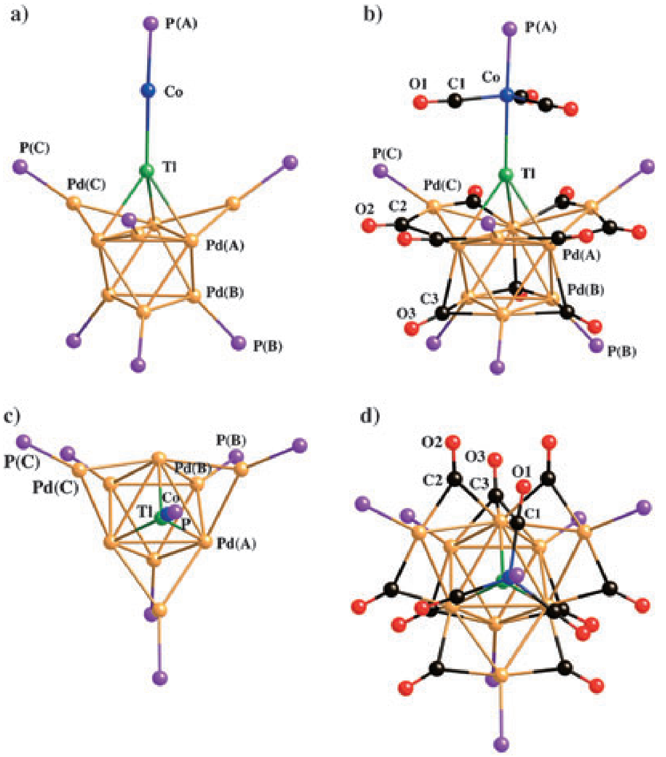

Figure 1. Side (a,b) and top views (b,c) of C_{3v} geometry of **1**: without CO ligands (a,c), and with CO ligands (b,d). The ethyl substituents are omitted for clarity.

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opposing triangular faces of the Pd_6 octahedron. The nine palladium atoms in **1** can be classified into three different types (A–C): namely, the three Pd(A) atoms of the "inner" Pd_3 triangle to which the $TlCo(CO)_3L$ ligand is attached, the three edge-bridging Pd(C) atoms, and the three Pd(B) atoms of the "outer" opposite (staggered) Pd_3 triangle in the Pd_6 octahedron (Figure 1 a). Of the seven phosphorus atoms, three are coordinated to the edge-bridging Pd(C) atoms, three to the Pd(B) atoms, and the remaining one (located on the pseudo threefold axis) to the cobalt atom (Figure 1 a,c). The 12 carbonyl ligands are distributed as follows: three terminal ones are connected to the cobalt atom, six doubly bridging ones are linked to the six Pd(C)–Pd(A) edges, and three triply bridging ones cap asymmetrically three alternate triangular faces of the Pd_6 octahedron (Figure 1 b, d). Mean distances and ranges of individual connectivities for both independent molecules under pseudo C_{3v} symmetry are given in Table 1.

Table 1: Selected mean interatomic distances for the two independent molecules of **1** under pseudo C_{3v} symmetry.

Bonding connectivity	N[a]	1st molecule		2nd molecule	
		Mean [Å]	Range [Å]	Mean [Å]	Range [Å]
Tl-Pd(A)	3	2.76	2.747(1)–2.775(1)	2.77	2.761(1)–2.798(1)
Tl···Pd(C)	3	3.33	3.262(1)–3.433(1)	3.28	3.197(1)–3.342(1)
Tl-Co	1	2.64	2.638(1)	2.64	2.643(1)
Pd(A)-Pd(C)	6	2.72	2.711(1)–2.733(1)	2.72	2.694(1)–2.728(1)
Pd(A)-Pd(A)	3	3.05	3.017(1)–3.089(1)	3.07	3.023(1)–3.088(1)
Pd(A)-Pd(B)	6	2.77	2.751(1)–2.788(1)	2.75	2.734(1)–2.785(1)
Pd(B)-Pd(B)	3	2.80	2.774(1)–2.821(1)	2.81	2.782(1)–2.820(1)
Pd(B)-P(B)	3	2.31	2.307(2)–2.329(2)	2.31	2.301(2)–2.315(2)
Pd(C)-P(C)	3	2.32	2.311(2)–2.331(2)	2.32	2.305(2)–2.321(2)
Co-P(A)	1	2.20	2.196(2)	2.20	2.199(2)
Pd(A)-(μ_2-CO)	6	2.09	2.070(6)–2.106(6)	2.09	2.076(5)–2.103(5)
Pd(C)-(μ_2-CO)	6	2.03	2.022(5)–2.032(5)	2.03	2.022(5)–2.051(5)
Pd(A)-(μ_3-CO)	3	2.31	2.262(5)–2.361(5)	2.32	2.304(5)–2.338(5)
Pd(B)-(μ_3-CO)	6	2.12	2.097(5)–2.134(5)	2.12	2.100(5)–2.144(5)
Co-CO	3	1.77	1.765(6)–1.776(6)	1.77	1.760(6)–1.771(6)
C-O	3	1.15	1.147(7)–1.158(7)	1.16	1.154(7)–1.165(6)
μ_2-C-O	6	1.16	1.151(7)–1.166(7)	1.16	1.148(6)–1.167(6)
μ_3-C-O	3	1.17	1.166(6)–1.175(6)	1.16	1.158(6)–1.168(6)

[a] N denotes the number of symmetry-equivalent connectivities under C_{3v} symmetry.

In marked distinction from the known Tl–Pd clusters, $[TlPd_6(CO)_6(PEt_3)_6]^+$[1a] and $[Tl_2Pd_{12}(CO)_9(PEt_3)_9]^{2+}$,[1b] in which each thallium(I) is coordinated to six palladium atoms in a conspicuously irregular manner with relatively long Tl–Pd bonds,[1c] the thallium(I) atom of the $TlCo(CO)_3PEt_3$ ligand in each of the two independent molecules of **1** is symmetrically coordinated to the three Pd(A) atoms with relatively short mean Tl–Pd(A) bonds of 2.76 and 2.77 Å. The much longer mean separations of 3.28 and 3.33 Å for the distances between Tl^{I} and the Pd(C) atoms of the edge-bridging $Pd(\mu_2\text{-}CO)_2L$ fragments are considered to be nonbonding (or weak secondary bonding) connectivities (Figure 1 a).

In cobalt carbonyl chemistry, the $TlCo(CO)_3L$ ligand of **1** represents the first X-ray characterized example of a trigonal-bipyramidal geometry about the central cobalt atom containing thallium(I) and phosphorus atoms (see below). The Tl-Co-P fragment in each independent molecule deviates only slightly (1.8° and 3.7°) from linearity, while the angular displacement of the Tl–Co bond from being perpendicular to the plane of the $Pd(A)_3$ triangle is 5.9° and 8.9°. The Tl–Co bond length is identical in the two independent molecules (2.64 Å) and compares favorably with the three Tl^{III}–Co bonds of 2.66 Å (average) found in the trigonal-planar $[Tl\{Co(CO)_4\}_3]$, which is the only reported structurally characterized compound containing discrete Tl–Co bonds.[6]

Table 1 shows that the Pd(A)–Pd(A) separations of the thallium-capped triangular face of the Pd_6 octahedron are 0.26 Å longer (average for both independent molecules) than the Pd(B)–Pd(B) separations of the opposite triangular face. This marked elongation may be attributed to the composite geometrical effect of the μ_3-$TlCo(CO)_3L$ and the three edge-bridging $Pd(\mu_2\text{-}CO)_2L$ ligations.

$^{31}P\{^1H\}$ NMR temperature-dependent spectra of **1** acquired at 11.74 T in $[D_8]$toluene solution[7] are shown in Figure 2. At room temperature (RT) three signals are displayed with an expected integral ratio of 3:3:1 in accordance with the solid-state structure. The observed and assigned signals at RT are as follows: a) a relatively narrow singlet (33 Hz) at 3.62 ppm attributed to the three P(B) nuclei; (b) a broad singlet (53 Hz) at 2.11 ppm attributed to the three P(C) nuclei;[8] and (c) a very broad doublet (≈360 Hz) at 96 ppm with $^2J_{P(A)\text{-}Tl} = 1800$ Hz unambiguously assigned to the P(A) atom axially coordinated to the cobalt atom. Upon the cooling of the toluene solution to −85 °C, the singlet at 2.11 ppm splits into a doublet with $^3J_{P(C)\text{-}Tl} = 180$ Hz, whereas the broad doublet arising from the cobalt-attached P(A) nucleus becomes narrowed by a factor of three to 105 Hz while its $^2J_{P(A)\text{-}Tl}$ coupling and chemical shift remain virtually unchanged, as shown in Figure 2. The narrowing observed with decreasing temperature follows the expected behavior for a spin $^1/_2$ nucleus J-coupled to a nucleus with a large electric quadrupolar moment.[9a] The splitting of the $\delta = 2.11$ ppm resonance, on the other hand, strongly suggests that the molecule is undergoing dynamic behavior.

A room-temperature $^{13}C\{^1H\}$ NMR spectrum (Figure 3), displays signals (in addition to those observed, but not shown in Figure 3, for $\text{-}CH_2\text{-}$ and $\text{-}CH_3$)[7] for all three types of CO carbon atoms: at $\delta = 247$ ppm for bridging μ_3-CO and 238 ppm assigned to μ_2-CO carbonyl groups coordinated to palladium atoms, and at $\delta = 212$ ppm for the three terminal, cobalt-bonded CO ligands. A decrease of the temperature to −60 °C broadens the $\delta = 212$ ppm signal to near coalescence, while further cooling to −85 °C splits it into a doublet ($^2J_{C\text{-}Tl} \approx$ 640 Hz). The size of this two-bond coupling is sensitivity to geometrical changes occurring in the sample arising from the dynamic behavior indicated by these data. The two-bond

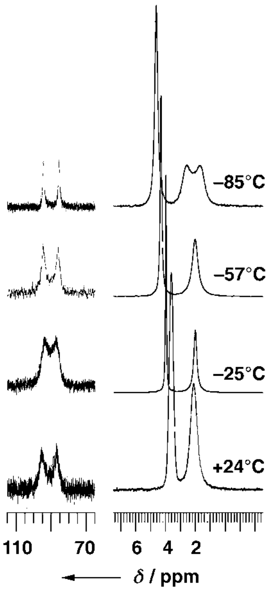

Figure 2. ^{31}P{^{1}H} spectra acquired at 202.5 MHz: number of transients = 100 to 400, repetition delay = 2 s, acquisition time = 0.64 s, line broadening = 3 Hz. The spectrum sections plotted for $\delta = 115–65$ ppm are vertically increased 70-fold.

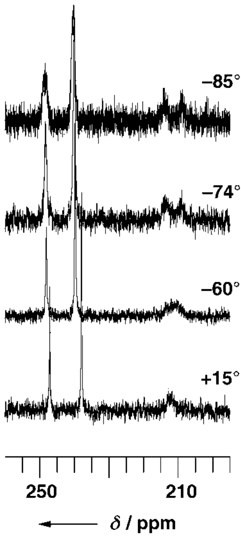

Figure 3. ^{13}C{^{1}H} spectra acquired at 125.8 MHz: number of transients = 1200 to 1800, repetition delay = 3 s, acquisition time = 0.95 s, line broadening = 4 Hz.

^{205,203}Tl-Co-^{31}P J-coupling, on the other hand, was observed to be essentially independent of these changes. The other carbonyl groups must have small two-bond J-coupling to the ^{205,203}Tl nuclei.

Extensive attempts to observe ^{205}Tl (or ^{203}Tl) signals at −85 °C over a wide range of chemical shifts, from −6000 ppm to +7500 ppm (relative to the ^{205}Tl signal readily observed in one scan from a 50 mM solution of $TlNO_3$ in D_2O used as a standard), were unsuccessful. Either the dynamic behavior observed in the ^{31}P and ^{13}C NMR spectra is in the broad coalescence region for ^{205,203}Tl, or the scalar-coupling broadening of the ^{205,203}Tl nuclei from the ^{59}Co nucleus is still large at −85 °C. Both may be present, as could other broadening mechanisms (beyond that expected from multiple ^{31}P splittings).[9b] The combination of these broadening mechanisms presumably prevents observation of ^{205,203}Tl resonances, even after 1000 scans.

The ^{31}P and ^{13}C NMR spectra provide strong evidence that **1** is undergoing dynamic behavior in toluene solution. This behavior is consistent with a model involving reversible dissociation/association of the $\mathrm{TlCo(CO)_3L}$ ligand from/to the Pd_9 core of **1** [Eq. (1)].

$$[\mathrm{Pd_9\{TlCo(CO)_3L\}(CO)_9L_6}] \rightleftharpoons [\mathrm{Pd_9(CO)_9L_6}] + [\mathrm{TlCo(CO)_3L}] \qquad (1)$$

At room temperature, the reversible conversion of these species is presumed to be fast on the NMR timescale. This proposed model of the rapid reversible dissociation/association of [$\mathrm{TlCo(CO)_3L}$] from the Pd_3 triangle of **1** in toluene appears to account for the temperature-dependent NMR data, even though it is surprising that the ^2J ^{31}P(A)-Co-Tl coupling constant and the ^{31}P(A) chemical shift remain essentially unchanged. The fact that the ^{31}P(A)-Tl ^2J coupling and chemical shift are not influenced by the temperature variation provides definitive NMR evidence that the cobalt-attached P(A) atom is not dissociating from the cobalt atom. The model rationalizes the changed ^{13}C signal of the three cobalt-attached carbonyl ligands, as well as the observed changes with the ^{31}P(C)-Tl ^3J coupling constants. The ^{31}P(B)-Tl ^3J value must be small.

Although the ^{31}P and ^{13}C NMR studies indicate that in solution the coordination of the [$\mathrm{TlCo(CO)_3L}$] ligand ($\mathrm{L = PEt_3}$) to the triangular $\mathrm{Pd(A)_3}$ face of the Pd_9 core is relatively weak, it must be, however, sufficiently strong to prevent disproportionation of this ligand into the corresponding $\mathrm{Tl^{III}}$ derivative and thallium metal [Eq (2)].

$$3\,[\mathrm{TlCo(CO)_3L}] \rightarrow [\mathrm{Tl\{Co(CO)_3L\}_3}] + 2\,\mathrm{Tl_{(S)}} \qquad (2)$$

The reaction in Equation (2) has been shown[2a] to be typical for $\mathrm{L = PR_3}$ with basicities close to and higher than that for PPh_3. In fact, no alkyl phosphine derivatives of [$\mathrm{TlCo(CO)_3(PR_3)}$] have been isolated to date.

An IR spectrum (THF) of **1** exhibited two characteristic terminal-carbonyl bands at 1974 (wm) cm^{-1} (A_1 mode) and 1910 (s) cm^{-1} (E mode) in accordance with the C_{3v} trigonal-bipyramidal geometry of [$\mathrm{TlCo(CO)_3L}$][2a,c] being maintained in solution. A solid-state IR spectrum (nujol) of **1** displayed analogous CO bands at 1974 (wm) 1912 (sh), and 1906 (s) cm^{-1} and thereby ruled out the occurrence of a possible disproportionation reaction [Eq. (2)] in THF solution.

While the NMR spectroscopic observations provide strong evidence for the dynamic behavior of **1** consistent with the proposed equilibrium process shown in Equation (1): namely the IR data show that this dynamic process in weakly polar THF solution is strongly weighted to one side of the equation, the left-hand side must be highly populated, to > 95 %; otherwise, the species on the right-hand side would be observed in the IR spectrum.[10]

A UV/Vis absorption spectrum of **1** (toluene) exhibited two electronic bands at approximately 314 and 428 nm. The 428 nm (visible-range) band may be a consequence of the expected strong ion-pair Tl–Co bonding interaction between Tl^I and $[Co(CO)_3L]^-$. Our assignment is based upon a detailed investigation of UV/Vis absorption spectra of $[TlCo(CO)_4]$ in different solvents by Schramm and Zink[4b] which led to their hypothesis that the presence of a band at wavelengths greater than 350 nm is indicative of $Tl^+[Co(CO)_4]^-$ ion-pair interactions; in particular, they observed that the UV/Vis absorption spectrum of $[TlCo(CO)_4]$ in toluene exhibits two characteristic bands at 283 and 435 nm.

Compound **1** (with $L = PEt_3$) can be prepared from either $[Pd_4(CO)_5L_4]$ (**2**) and/or $[Pd_{10}(CO)_{12}L_6]$ (**3**) with $[TlCo(CO)_4]$ in THF, C_6H_6, or C_7H_8 solutions at room or elevated temperatures. In the case of only **2** being involved in the reaction, an excess of the undesired phosphine L ligand would be generated, which in turn would trigger the formation of $[Tl\{Co(CO)_3L\}_3]$ and thallium metal by the disproportionation reaction [Eq. (2)], as ideally formulated in Equation (3).

$$\begin{aligned}27\,[Pd_4(CO)_5L_4] + 36\,[TlCo(CO)_4] \rightarrow\\ 12\,[Pd_9\{TlCo(CO)_3L\}(CO)_9L_6]+\\ 8\,[Tl\{Co(CO)_3L\}_3] + 16\,Tl_{(s)} + 63\,CO\end{aligned} \tag{3}$$

On the other hand, the reaction with only **3** as the other reactant would instead give rise to the formation of palladium metal owing to the deficiency of L, as ideally formulated in Equation (4).

$$\begin{aligned}7\,[Pd_{10}(CO)_{12}L_6] + 6\,[TlCo(CO)_4] \rightarrow\\ 6\,[Pd_9\{TlCo(CO)_3L\}(CO)_9L_6] + 16\,Pd_{(s)} + 36\,CO\end{aligned} \tag{4}$$

To optimize the yield of **1**, we set the mole ratio Pd/L of the reactants to be 9/7, and thereby combined both Equations (3) and (4) to give the idealized stoichiometry in Equation (5) for the reaction. This reaction[11] was carried

$$\begin{aligned}9\,[Pd_{10}(CO)_{12}L_6] + 16\,L + 10\,[TlCo(CO)_4] \rightarrow\\ 10\,[Pd_9\{TlCo(CO)_3L\}(CO)_9L_6] + 28\,CO\end{aligned} \tag{5}$$

out in two stages: 1) an initial reaction of **3** and L under CO with formation in situ of a required ratio of **2** and **3**;[12] and 2) a subsequent reaction of this mixture with a stoichiometric amount of $[TlCo(CO)_4]$.[3c]

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[5] a) X-Ray data for crystal of **1** were collected at 100(2) K on a Bruker SMART CCD-1000 area-detector diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) from a sealed-tube generator. The crystal structure was determined from direct methods. Least-squares refinements (based on F^2) were carried out with SHELXTL.[5b] CCDC-240814 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). $[Pd_9\{TlCo(CO)_3PEt_3\}(CO)_9(PEt_3)_6]$: $M_r = 2384.07$, monoclinic, $P2_1/c$, $a = 14.584(1)$, $b = 44.101(2)$, $c = 23.589(1)$ Å, $\alpha = \gamma = 90$, $\beta = 91.388(1)°$, $V = 15\,166.9(9)$ Å^3, $Z = 8$; $F(000) = 9216$; $\rho_{calcd} = 2.088\ Mg\,m^{-3}$. 146406 reflections were obtained over $1.96 \leq \theta \leq 56.6°$. Empirical absorption correction (SADABS) was applied ($\mu(Mo_{K\alpha}) = 4.605\ mm^{-1}$, max./min. transmission, 0.7697/0.4045). Full-matrix least-squares refinement (on F^2) of 37250 independent merged reflections $R(int) = 0.0443$ with 1515 parameters (21 restraints) converged at $wR_2(F^2) = 0.0860$ for all data; $R_1(F) = 0.0315$ for $I > 2\sigma(I)$; max./min. residual electron density, 1.90/−1.16 eÅ^{-3}; GoF (on F^2) = 0.884. Hydrogen atoms were included in structure factor calculations at idealized positions and were allowed to ride on attached carbon atoms with relative isotropic displacement coefficients. All non-hydrogen atoms, except carbon atoms of disordered CH_2 and CH_3 groups, were refined anisotropically; b) all crystallographic software and sources of the scattering factors are contained in the SHELXTL (version 5.1; G. Sheldrick) program library, Bruker Analytical X-Ray Systems, Madison, WI; c) Superposition of the refined positional parameters for the corresponding 11 metal atoms in the two crystallographically independent molecules showed their geometries to be nearly equivalent, as evidenced by the weighted rms deviation of 0.091 Å for the optimal superimposed fit.[5b] Hence, it was necessary to determine that they are not related to each other by a higher symmetry space group. Structural tests, performed by the checkcif@iuer.org service with check CIF/PLATON, provided convincing evidence that the uniquely determined centrosymmetric monoclinic $P2_1/c$ space group was indeed correctly chosen.

[6] J. W. van Hal, L. B. Alemany, K. H. Whitmire, *Inorg. Chem.* **1997**, *36*, 3152.

[7] NMR spectra were obtained for C_7D_8 solutions of **1** under N_2 atmosphere on Bruker AC-300 or Varian UNITY-500 and INOVA-500 spectrometers. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were referenced, respectively, to TMS by the ^1H signal of residual protons of [D$_8$]toluene at 2.09 ppm, to TMS by the methyl ^{13}C signal of [D$_8$]toluene at 20.4 ppm, and to 85 % H_3PO_4 in D_2O as an external standard (at 300 MHz). At 500 MHz, the unified-scale method of referencing ["*NMR Nomenclature. Nuclear Spin Properties and Conventions for Chemical Shifts*"

(IUPAC Recommendations 2001): R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795–1818] was used for referencing ^{13}C, ^{31}P, ^{205}Tl, and ^{203}Tl from the ^{1}H-TMS reference. ^{1}H NMR (300 MHz, ambient temperature): $\delta_1 = 0.81$ ppm (dt, 9H, CH_3, $^3J_{H\text{-}H} = 7.8$ Hz, $^3J_{H\text{-}P} = 15.7$ Hz); $\delta_2 = 0.94$ ppm (dt, 27H, CH_3, $^3J_{H\text{-}H} = 7.5$ Hz, $^3J_{H\text{-}P} = 15.0$ Hz); $\delta_3 = 1.06$ ppm (dt, 27H, CH_3, $^3J_{H\text{-}H} = 7.6$ Hz, $^3J_{H\text{-}P} = 15.2$ Hz); $\delta_4 = 1.42$ ppm (qn, 6H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.9$ Hz); $\delta_5 = 1.56$ ppm (qn, 18H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.4$ Hz); $\delta_6 = 1.74$ ppm (qn, 18H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.4$ Hz) with intensity ratios of $\delta_1/\delta_2/\delta_3/\delta_4/\delta_5/\delta_6/ = 1.04/3.00/2.98/0.67/1.94/1.94$ (versus theoretical ones of 1.00/3.00/3.00/0.67/2.00/2.00). ^{1}H (500 MHz, −25 °C): $\delta_1 = 0.81$ ppm (dt, 9H, CH_3, $^3J_{H\text{-}H} = 7.8$ Hz, $^3J_{H\text{-}P} = 15.7$ Hz); $\delta_2 = 0.94$ ppm (dt, 27H, CH_3, $^3J_{H\text{-}H} = 7.5$ Hz, $^3J_{H\text{-}P} = 14.6$ Hz); $\delta_3 = 1.06$ ppm (dt, 27H, CH_3, $^3J_{H\text{-}H} = 7.6$ Hz, $^3J_{H\text{-}P} = 14.6$ Hz); $\delta_4 = 1.36$ ppm (qn, 6H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.7$ Hz); $\delta_5 = 1.58$ ppm (qn, 18H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.4$ Hz); $\delta_6 = 1.74$ ppm (qn, 18H, CH_2, $^3J_{H\text{-}H} = {}^2J_{H\text{-}P} = 7.4$ Hz) with intensity ratios of $\delta_1/\delta_2/\delta_3/\delta_4/\delta_5/\delta_6/ = 1.09/2.98/3.13/0.77/1.95/2.01$ (versus theoretical ones of 1.00/3.00/3.00/0.67/2.00/2.00). ^{1}H (500 MHz, −85 °C): $\delta_1 = 0.80$ ppm (barely resolved dt); $\delta_2 = 0.93$ ppm (barely resolved dt); $\delta_3 = 1.01$ ppm (barely resolved dt); $\delta_4 = 1.25$ ppm (broad single peak, half-width at half height = 17 Hz); $\delta_5 = 1.57$ ppm (broad single peak, half-width at half height = 19 Hz); $\delta_6 = 1.71$ ppm (broad single peak, half-width at half height = 17 Hz). ^{13}C{^{1}H} (125.797 MHz at 15 °C): $\delta = 7.91$ (s, 3C, CH_3); 8.29 (s, 9C, CH_3); 8.64 (s, 9C, CH_3); 16.14 (d, 9C, CH_2, $^1J_{C\text{-}P} = 18.6$ Hz); 16.71 (d, 9C, CH_2, $^1J_{C\text{-}P} = 14.1$ Hz); 22.08 (d, 3C, CH_2, $^1J_{C\text{-}P} = 22.0$ Hz); 212 (s, 3C, terminal CO); 238 (s, 6C, μ_2-CO); 247 ppm (s, 3C, μ_3-CO). ^{31}P{^{1}H} (202.513 MHz), RT: $\delta = 2.11$ (s, 3P, P(C)), 3.62 (s, 3P, P(B)), 96 ppm (d, 1P, $^2J_{P\text{-}Tl} = 1800$ Hz, P(A)); −85 °C: $\delta_1 = 2.14$ (d, 3P, P(C), $^3J_{P(C)\text{-}Tl} = 180$ Hz), $\delta_2 = 4.63$ (s, 3P, P(B)), $\delta_3 = 95$ ppm (d, 1P, $^2J_{P\text{-}Tl} = 1800$ Hz) with ratio of intensities $\delta_1/\delta_2/\delta_3 = 3.0/3.0/1.0$.

[8] The three P(C) nuclei in the non-dissociated structure of **1** (in solution) should be comparatively closer to the Tl atom (i.e., the mean nonbonding P(C)···Tl separation in the solid-state structure is 5.06 Å versus the mean P(B)···Tl separation of 6.77 Å). In addition, each P(C) atom may interact with Tl not only by ^3J coupling through the P(C)-Pd(C)-Pd(A)-Tl bonding chain but also more directly by ^2J coupling through a P(C)-Pd(C)···Tl shorter link including secondary bonding interactions.

[9] a) "Chemical and Biochemical Applications" by R. G. Kidd in *NMR of Newly Accessible Nuclei*, *Vol. 1* (Ed.: P. Laszlo), Academic Press, New York, **1983**, pp. 123–125; b) Quadrupolar coupling with the ^{59}Co nucleus ($I = 7/2$, 100%; $Q = 42.0$ fm^2) can broaden the thallium line shape through scalar coupling relaxation, but not through the commonly understood method of direct splitting of the resonance by scalar coupling. ^{59}Co has a very large electric quadrupole moment (147 × that of ^{2}H) and should therefore self-decouple unless the ^{59}Co nucleus is in a very symmetric bonding arrangement (either tetrahedral or octahedral). Self-decoupling occurs when the relaxation time for transitions between the available spin states (namely, eight for ^{59}Co with $I = 7/2$) will be so fast that other nuclei will only see the "average" spin state from ^{59}Co. Since the ^{59}Co nucleus in **1** has a trigonal-bipyramidal ligand environment, its relaxation should be very fast such that it should have no direct coupling (splitting of resonances) with other nuclei. Other nuclei, even so, can be broadened by a scalar coupling relaxation mechanism with cobalt that typically will increase the transverse relaxation rate (decrease the line width) as the temperature is decreased. This narrowing of the resonances as the temperature is decreased are clearly observed in the ^{31}P spectra of Figure 2. The same narrowing is not observed in the ^{13}C spectra of Figure 3, however. In this case, the line widths in the ^{13}C NMR spectrum are dominated by exchange broadening.

[10] The fact that IR frequencies are very fast ($\approx 10^{13}$ s^{-1}) implies that the solution IR carbonyl spectrum should give rise to the superposition of vibrational signals from all species (as though static) generated in solution. The presence of two observed frequencies at 1912 and 1906 cm^{-1} in the solid state versus one at 1910 cm^{-1} in THF may be readily attributed to factor-group splitting of the E vibrational mode under the monoclinic crystal packing environment. Hence, the remarkable agreement in the solution/solid-state IR spectra of the corresponding terminal and bridging carbonyl frequencies provides no observable evidence for a rapid detachment/reattachment process of either the entire [$TlCo(CO)_3PEt_3$] ligand or its PEt_3 group; in either case the cobalt-attached terminal carbonyl frequencies would be noticeably shifted.

[11] Reactions were carried out by standard Schlenk techniques on a preparative vacuum line under nitrogen atmosphere. All solvents were deoxygenated by the bubbling of N_2 through them for at least 20 min at room temperature. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer by use of CaF_2 windows or a nitrogen-purged CaF_2 cell. [$TlCo(CO)_4$] was prepared according the procedure of Schussler et al.[3c] The synthesis of [$Pd_{10}(CO)_{12}L_6$] (**3**) is analogous to that of [$Pd_{10}(CO)_{12}(PnBu_3)_6$];[12] compound **3** was purified by recrystallization from C_6H_6/heptane. A typical procedure for the preparation of **1**: a solution of [$Pd_{10}(CO)_{12}(PEt_3)_6$] (0.400 g; 0.190 mmol) and PEt_3 (0.05 mL; 0.344 mmol) in toluene (8 mL) was stirred for about 10 min at RT under CO. The atmosphere was changed to N_2, after which [$TlCo(CO)_4$] (0.135 g; 0.360 mmol) was added under continued stirring for 45 min. at 70 °C. The resulting deep-brown-yellowish solution was filtered to remove a black precipitate, heptane (6 mL) was added to the filtrate, and the solution was kept overnight at −20 °C. Black crystals of **1**, (0.113 g) were collected (from the solution which also contained a small amount of light amorphous brown precipitate) and then were washed with hexane. The solution was filtered, heptane (30 mL) was added to the filtrate, and an additional 0.092 g of crystals of **1** were separated by the above procedure, in this case without formation of any amorphous precipitate. Total yield of **1** was 0.205 g (41% on the basis of Pd). IR spectra in Nujol: 1974 (wm), 1912 (sh), 1906 (s), 1878 (s), 1852 (m), 1835 (sh w), 1794 (m), 1761 (ms) cm^{-1}; in THF solution: 1974 (wm), 1910 (s), 1881 (s), 1852 (mw), 1801 (ms), 1770 (s) cm^{-1}. Single crystals of **1** were obtained by vapor diffusion of pentane into toluene solution of **1**; one of size $0.24 \times 0.09 \times 0.06$ mm^3 was used for the X-ray diffraction study.

[12] For such a Pd/L ratio with the PEt_3 ligand under CO atmosphere, it was shown that only palladium clusters of nuclearity $n = 4$ and 10 exist: E. G. Mednikov, N. K. Eremenko, *Izv. Acad. Nauk Ser. Khim.* **1982**, 2540; [*Bull. Acad. Sc. USSR Div. Chem. Sc.* **1982**, *31*, 2240 (Engl. Transl.)].