Bis(tetramethylthiophene)ruthenium(0) and its iron tetracarbonyl adduct

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3e was obtained. Colorless crystals of **3e** suitable for X-ray diffraction were grown by slow cooling in hexane at −15 °C.[13] The resulting structure shows slight rotational disorder about one of the Pd–Si bonds, which was successfully modeled by refining two conformeric structures in an approximately 3:1 ratio. The ORTEP diagram of the major conformer is shown in Figure 1 along with significant bond lengths and angles. The coordination of the palladium is nearly square planar with a slight twist of 2°. The two methyl groups on each silicon atom lie above and below the central square plane and are directed away from the phosphine ligand by the bulky cyclohexyl groups. The Si–Pd bond lengths of 2.3563 (9) and 2.359 (1) Å are within known values of Si–Pt bond lengths in analogous complexes (2.354–2.423 Å)[14,15] but significantly shorter than Sn–Pd bond lengths (2.563–2.585 Å).[16]

Bis(silyl)palladium complexes have been implicated as important intermediates in the palladium-catalyzed bis-silylation of acetylenes,[2] dienes,[3] and isonitriles[4] by disilanes; however, little is directly known about the reactivity of these species. A four-step catalytic cycle for the bis-silylation of acetylenes has been proposed in which (1) the disilane adds to the metal center to afford a bis(silyl)metal complex, (2) the bis(silyl) complex coordinates with the acetylene, (3) the coordinated acetylene inserts into a silicon–metal bond to give a vinylmetal complex, and (4) reductive elimination occurs to release the *cis*-olefin and regenerate the catalytic species.[2e] Since we have already demonstrated that disilanes may react with an appropriate palladium precursor to give stable bis(silyl) species (step 1), it was of interest to examine the subsequent reactivity of these palladium bis(silyl) compounds toward acetylenes and their role in catalytic bis-silylation. The palladium bis(silyl) species **3e** was thus found to react stereospecifically with 2.5 equiv of $MeO_2CC{\equiv}CCO_2Me$ at 25 °C to cleanly afford dimethyl *cis*-bis(dimethylsilyl)maleate (**4**) and the palladium π-complex of the alkyne (**5**; Scheme I). These results provide the first experimental verification of the reaction of a palladium bis(silyl) compound with an acetylene to produce a bis-silylated olefin and thereby lend strong support for steps 2–4 in the proposed mechanism.[17] The Pd(0) species which is produced after the reductive elimination (step 4) is apparently scavenged by excess acetylene to afford the π-complex **5**.[18] The complex **3e** also participates in the catalytic bis-silylation of the alkyne: reaction of $HMe_2SiSiMe_2H$ with $MeO_2CC{\equiv}CCO_2Me$ in the presence of catalytic **3e** (2 mol %, 80 °C, 2 h) affords the *cis* olefin **4** in 45% yield. The reactivities of palladium bis(silyl) species toward other organic substrates are currently being investigated.

Acknowledgment. We thank the Tulane Center for Bioenvironmental Research and the Tulane Committee on Research for support of this work. We also thank Dr. Deborah A. Grimm of the Tulane University Coordinated Instrumentation Facility for assistance with mass spectral data.

Supplementary Material Available: Tables of experimental crystallographic data, positional and thermal parameters, bond lengths and angles, root-mean-square amplitudes, and least-squares planes for **3e** (13 pages). Ordering information is given on any current masthead page.

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(13) Crystal data: dimensions 0.23 × 0.43 × 0.53 mm; crystal system monoclinic; space group $P2_1/n$; a = 12.327 (1) Å; b = 17.557 (2) Å; c = 16.634 (3) Å; β = 102.39 (1)°; Z = 4; absorption coefficient 6.9 cm^{-1}; Mo Kα radiation with graphite monochromator; 2θ range 1.0–48.0°, 5502 unique reflections with 4282 $\geq 3\sigma(I)$. The structure was solved by Patterson methods and refined to convergence with R = 0.027 and R_w = 0.040.

(14) (a) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 1369–1371. (b) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219–1221. The related complex (dcpe)Pt$(SiH_2Me)_2$ shows a Pt–Si bond length of 2.354 (2) Å (results to be submitted for publication).

(15) Mullica, D. F.; Sappenfield, E. L.; Hampden-Smith, M. J. *Polyhedron* **1991**, *10*, 867–872.

(16) (a) Mason, R.; Whimp, P. O. *J. Chem. Soc. A* **1969**, 2709–2717. (b) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193–198.

(17) A similar reaction has been recently observed for a platinum bis(silyl) complex with phenylacetylene: Tanaka, M.; Uchimaro, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16–18.

(18) Characterization for **5**: mp 142 °C dec; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 65.9 (s); ^1H NMR (δ, C_6D_6) 1.09–1.98 (48 H, featureless resonance), 3.50 (6 H, s); $^{13}C\{^1H\}$ NMR (δ, C_6D_6) 22.29 (dd, dcpe), 26.33 (s, dcpe), 27.30 (d, dcpe), 29.34 (s, dcpe), 29.87 (d, dcpe), 34.99 (d, dcpe), 51.92 (s, CH_3), 111.94 (AA′X, $^2J_{C-P(cis)} + {^2J_{C-P(trans)}}$ = 73.8 Hz, $-C{\equiv}$), 168.00 (AA′X, $^3J_{C-P(cis)} + {^3J_{C-P(trans)}}$ = 32.6 Hz, C=O); IR (KBr, cm^{-1}) 1797 (w, $\nu(C{\equiv}C)$), 1696 (vs, $\nu(C{=}O)$); MS (EI, 70 eV) m/z 670 (M^+, 5%), 611 (M^+ − COOMe, 5), 528 (M^+ − MeOOCC≡CCOOMe, 100). Anal. Calcd for $C_{32}H_{54}O_4P_2Pd$: C, 57.27; H, 8.11. Found: C, 56.81; H, 7.99.

Bis(tetramethylthiophene)ruthenium(0) and Its $Fe(CO)_4$ Adduct

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Summary: Reduction of $[Ru(\eta^5\text{-}C_4Me_4S)_2](OTf)_2$ (C_4Me_4S is 2,3,4,5-tetramethylthiophene, OTf is $CF_3SO_3^-$) at −78 °C with 2 equiv of Cp_2Co gives $Ru(C_4Me_4S)_2$ (**1**), which is stable at <−20 °C. DNMR studies suggest that **1** is fluxional as a result of the facile interconversion of η^5-C_4Me_4S and η^4-C_4Me_4S ligands. In contrast, $(\eta^5\text{-}C_4Me_4S)Ru\{(\eta^4{:}\eta^1\text{-}C_4Me_4S)Fe(CO)_4\}$, prepared from **1**, $Fe(CO)_5$, and Me_3NO, is thermally stable and adopts a static structure. In the solid state, **1**·$Fe(CO)_4$ adopts a symmetric structure such that the two pairs of C=C groups are eclipsed.

As an extension of our recent work on ruthenium(0) derivatives of thiophenes,[1] we have prepared the first homoleptic M(0) thiophene complex.[2] This new compound is of interest from a number of perspectives, not the least of which is its possible relationship to the interaction of thiophenes with metal surfaces.[3] The present report is concerned with proof of structure and physical

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(1) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.*, in press.

(2) Review: Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

(3) (a) Cocco, R. A.; Tatarchuk, B. J. *Surf. Sci.* **1989**, *218*, 127. (b) Heise, W. H.; Tatarchuk, B. J. *Surf. Sci.* **1989**, *207*, 297.

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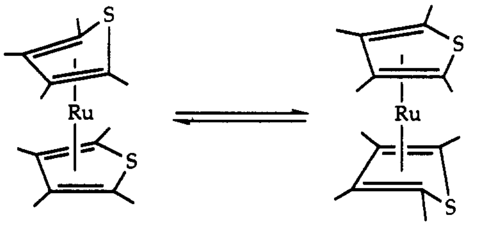
properties of this unstable compound.

Yellow crystals of $Ru(C_4Me_4S)_2$ (1) were obtained by cobaltocene reduction of THF solutions of $[Ru(\eta^5\text{-}C_4Me_4S)_2](OTf)_2$ at low temperatures according to eq 1.[4]

$$[Ru(C_4Me_4S)_2]^{2+} + 2Cp_2Co \xrightarrow{-20\ °C} Ru(C_4Me_4S)_2 + 2Cp_2Co^+ \quad (1)$$

Samples of 1 are stable at room temperature both in the solid state and in Et_2O solutions ($t_{1/2} \approx 10$ min), although its toluene solutions must be maintained below −20 °C. Interestingly, thermal decomposition (toluene solution, 25 °C) affords only 13% free C_4Me_4S. Our previous attempt to prepare 1 did not account for this thermal instability.[5] Signals arising from C_4Me_4S and its fragments dominate its 70-eV electron impact mass spectrum; however, a weak molecular ion envelope was observed.

The ^1H NMR spectrum of 1 (THF-d_8) shows only two singlets at 1.73 and 1.65 ppm and is invariant from +20 to −90 °C (500 MHz). At room temperature separate signals can be observed for 1 and free C_4Me_4S; thus, the dynamic process is not dissociative. The ^{13}C NMR spectrum is also extremely simple down to −90 °C, consisting of four signals. The chemical shifts (91.55, 64.45 ppm) for the ring carbon atoms α and β with respect to sulfur occur near the average (90.5, 63.5 ppm) of the chemical shifts for C_α and C_β in η^5- (~96, 89 ppm) and η^4-thiophene ligands (~85, 38 ppm).[6] These data indicate a fluxional structure involving rapid attachment and detachment of the Ru–S bonds (eq 2).



(2)

We estimate that the free energy of activation for the inversion process in eq 2 is <27 kJ/mol, based on the ^{13}C NMR shifts for pairs of η^4- and η^5-C_4R_4S complexes.[7] In contrast, the corresponding fluxionality for $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ is easily frozen on the NMR time scale, since it is subject to a relatively large barrier ($\Delta G^\ddagger = 67.8$ kJ/mol).[8] The disparate dynamic properties of the bis(thiophene)- and bis(arene)ruthenium(0) complexes correlate with their differing reduction potentials. $[Ru(C_4Me_4S)_2]^{2+}$ undergoes two 1e reductions at $E_{1/2} = -392$ and −568 mV, while 2e reduction of $[Ru(C_6Me_6)_2]^{2+}$ occurs at −976 mV (vs Ag/AgCl).[9] Both $E_{1/2}$[10] and $\Delta G^\ddagger$ are related to a reorganization energy which is a measure of the ease of the ring (thiophene or arene) folding processes. We propose that the decreased folding barrier for the thiophene complex is a reflection of the decreased resonance energy of the free ligand.[11]

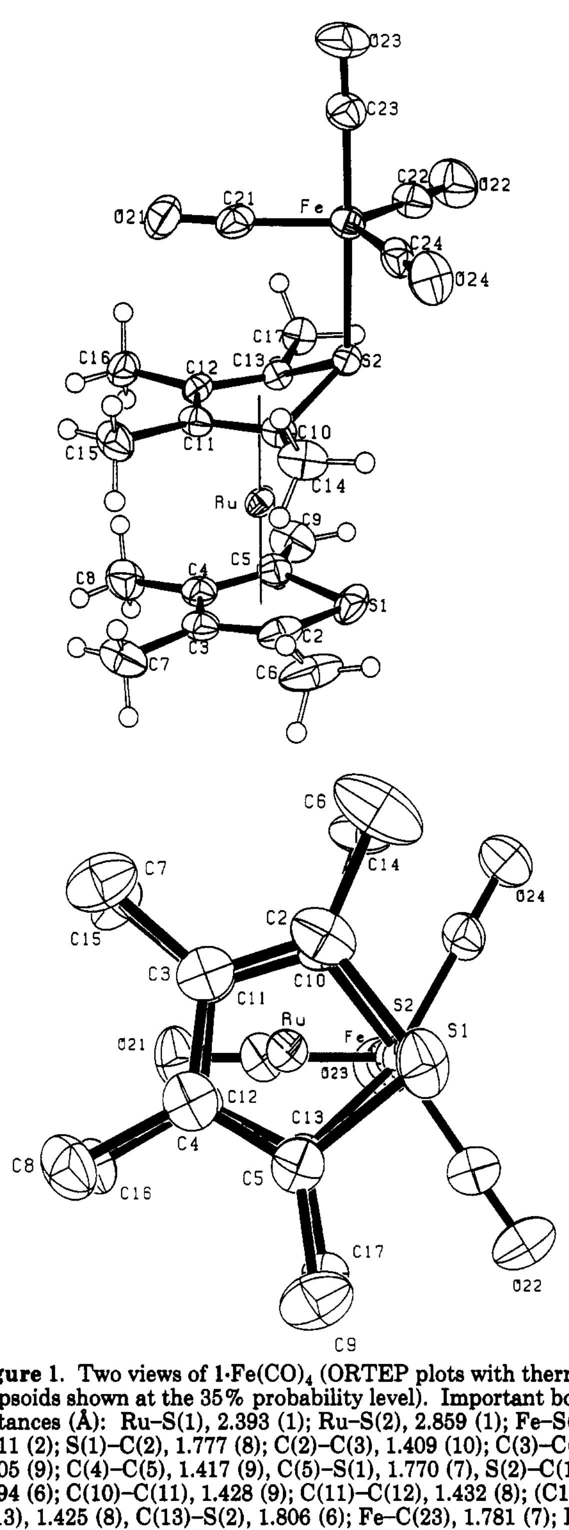


Figure 1. Two views of 1·$Fe(CO)_4$ (ORTEP plots with thermal ellipsoids shown at the 35% probability level). Important bond distances (Å): Ru–S(1), 2.393 (1); Ru–S(2), 2.859 (1); Fe–S(2), 2.311 (2); S(1)–C(2), 1.777 (8); C(2)–C(3), 1.409 (10); C(3)–C(4), 1.405 (9); C(4)–C(5), 1.417 (9), C(5)–S(1), 1.770 (7), S(2)–C(10), 1.794 (6); C(10)–C(11), 1.428 (9); C(11)–C(12), 1.432 (8); (C12)–C(13), 1.425 (8), C(13)–S(2), 1.806 (6); Fe–C(23), 1.781 (7); Fe–C(21), 1.799 (7); Fe–C(22), 1.801 (7); Fe–C(24), 1.802 (7). Important bond angles (deg): C(2)–S(1)–C(5), 90.6 (3); C(10)–S(2)–C(13), 84.7 (3); S(2)–Fe–C(23), 176.7 (2).

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[4] To a THF slurry of 0.500 mg (0.735 mmol) of $[Ru(C_4Me_4S)_2](OTf)_2$ was added to 2 equiv of solid Cp_2Co at −78 °C. After 3 h, the reaction mixture was warmed to −20 °C and evaporated. The yellow residue was extracted into −20 °C Et_2O, and this mixture was filtered. Removal of solvent gave yellow microcrystals. ^1H NMR (500 MHz, THF-d_8, −90 °C): 1.73, 1.65 ppm. ^{13}C NMR (125 MHz, THF-d_8, −90 °C): 91.55, 64.45, 15.42, 12.24 ppm. FDMS: m/z 382 (M^+, 0.3%).

[5] Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828.

[6] ^{13}C NMR shift data for η^4-thiophene ligands: Luo, S.; Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 1732.

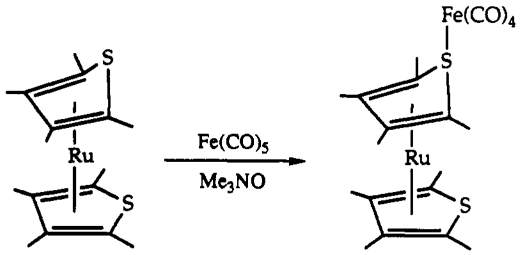
[7] This $\Delta G^\ddagger$ value is an underestimate, since it is calculated for a coalescence temperature of −90 °C (for a two-site exchange of the α-carbon signals with a $\Delta\nu$ value of 6375 Hz or 51 ppm). $\Delta G^\ddagger$ (in kJ/mol) was calculated from the equation $19.14(10.32 + \log(T_c/k_c))$, where $2.22(\Delta\nu) = k_c$, the exchange rate (in s^{-1}) at the coalescence temperature (T_c): Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, Germany, 1991; Chapter 11.

[8] Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 7425. $\Delta G^\ddagger$ for $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ was calculated from the Darensbourg and Muetterties data at −90 °C for $\Delta H^\ddagger = 67.4$ kcal/mol and $\Delta S^\ddagger = -12.6$ cal/(K·mol).

[9] Price, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7636. Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084.

[10] This assumes that $\Delta E_{1/2}$ and $\Delta E°$ values are closely related.

The assignment of 1 as $Ru(\eta^4\text{-}C_4Me_4S)(\eta^5\text{-}C_4Me_4S)$ is supported by the synthesis of its brown-orange, thermally stable $Fe(CO)_4$ adduct (eq 3). The 400-MHz ^1H NMR spectrum (20 °C) of $1{\cdot}Fe(CO)_4$ showed four equally intense singlets, as expected for a static structure.[12] The average of ^{13}C NMR chemical shifts for $1{\cdot}Fe(CO)_4$ corresponds to those seen for 1.



(3)

The crystallographic study confirmed that $1{\cdot}Fe(CO)_4$ is described as $(\eta^5\text{-}C_4Me_4S)Ru\{\eta^4{:}\eta^1\text{-}C_4Me_4S(Fe(CO)_4)\}$, which adopts a symmetric structure with an approximate symmetry plane containing atoms Ru, Fe, S(1), and S(2) (Figure 1).[13] The two pairs of C═C groups are nearly eclipsed, as are the iron, two sulfur atoms, and one CO. The $\eta^5\text{-}C_4Me_4S$ ring and the diene portion of the $\eta^4{:}\eta^1\text{-}C_4Me_4S$ are nearly mutually parallel with a dihedral angle of only 1.5°. The slightly shorter Ru–C distances for the $\eta^4{:}\eta^1\text{-}C_4Me_4S$ portion of the molecule suggests that this ligand is the better electron acceptor. For the $\eta^4{:}\eta^1\text{-}C_4Me_4S$ ligand the S atom is bent out of the diene-like plane with a dihedral angle (between C10–C13 and C10–S2–C13) of 32.1°.[14]

In summary, we have succeeded in isolation of the thiophene analogue of Fischer's classic $Ru(\eta^4\text{-}C_6Me_6)(\eta^6\text{-}C_6Me_6)$.[15] The new species differs from the hexamethylbenzene complex in that it is highly fluxional and unstable thermally. Its fluxional character is indicative of the increased pliability of heterocyclic ligands. Its instability is almost certainly related to the decomposition of thiophenes on Ru surfaces even at 120 K[3] and possibly the metal-catalyzed desulfurization of thiophenes.[16] Further studies are underway on the reactivity of 1 and related Ru(0) thiophene complexes.

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Supplementary Material Available: For $1{\cdot}Fe(CO)_4$, tables of crystal parameters and intensity collection data, bond distances and angles, and positional and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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[11] The following resonance energy values for the π-ligands discussed herein are given in the literature (kJ/mol): C_6H_6 (150);[11a] C_6Me_6 (109–138);[11b] C_4H_4S (84–121).[11a] (a) Cook, M. J.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem.* **1974**, *17*, 255. (b) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 98.

[12] A THF solution of 1, prepared from 170 mg (0.250 mmol) of $[Ru(C_4Me_4S)_2](OTf)_2$ with 97.5 mg (0.516 mmol) of Cp_2Co at −78 °C, was treated with 59.6 mg (0.304 mmol) of $Fe(CO)_5$ and 20.6 mg (0.274 mmol) of Me_3NO. After 4 h, the yellow solution was warmed to room temperature and evaporated and the residue extracted with toluene. Evaporation of the toluene extract afforded 114 mg of brown-orange crystals (83% based on $[Ru(C_4Me_4S)_2](OTf)_2$). Anal. Found (calcd) for $C_{20}H_{24}FeO_4RuS_2$: C, 43.78 (43.72); H, 4.48 (4.40); S, 11.66 (11.67). ^1H NMR (400 MHz, C_6D_6, 20 °C): 1.51, 1.48, 1.25, 0.95 ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): 217.20, 96.24, 89.42, 83.44, 54.90, 14.04, 12.75, 12.25, 10.41 ppm. FDMS: m/e 550 (M^+ for ^{102}Ru and ^{56}Fe). IR (KBr, ν_{CO}): 2014 (s), 1980 (m), 1923 (s), 1903 (s) cm^{-1}.

[13] Crystals of $1{\cdot}Fe(CO)_4$ were grown from toluene: Syntex $P2_1$, Mo Kα, numerical adsorption correction; ω scan; Ru, Fe, S, O, and C anisotropic; lattice constants (253 K) $a = 1056.4$ (2) pm, $b = 1267.5$ (3) pm, $c = 1708.8$ (8) pm, $\alpha = \beta = \gamma = 90°$, $V = 2288 \times 10^6$ pm^3; orthorhombic, $P2_12_12_1$ (No. 19); $Z = 4$; μ(Mo Kα) = 14.78 cm^{-1}; profile analysis $2\theta_{max} = 50.0°$, 2228 reflections, 2111 with $I > 2.58\sigma(I)$, 349 parameters, $R = 0.030$, $R_w = 0.039$.

[14] As described in ref 2, several examples of $\eta^4{:}\eta^1\text{-}C_4R_4S$ complexes are known; recent reports: Luo, S.; Ogilvy, A. E.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002. Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2438.

[15] Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162. $Ru(C_6H_6)_2$, characterized only by ^1H NMR spectroscopy, decomposes below 0 °C to give a "brown solid": Timms, P. L.; King, R. B. *J. Chem. Soc., Chem. Commun.* **1978**, 898.

[16] Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1991. Reynolds, J. G. *Chem. Ind.* **1991**, 570.

Clusters as Ligands. Stabilization of a Cd_3Co Core in $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$

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Summary: The reaction of the cluster ligand precursor $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ with $Cd(CH_3)_2$ yields $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$, 1, as one of the reaction products. Crystallographic characterization shows a triangular Cd_3 core capped with a $Co(CO)_3$ fragment and edge-bridged with three cluster carboxylate ligands. The presence or absence of a Cd–Cd bond is subject to interpretation. It is argued that the most reasonable description of the cadmium centers is as Cd^+.

We have pointed out the advantages of considering a transition metal cluster as a bulky substituent with unusual electronic properties.[1] In principle, joining a transition metal cluster to a ligand functionality permits the construction of clusters of clusters based on established coordination geometries of cationic metal centers. Our work to date based on this idea also demonstrates that a cluster substituent can significantly change the character of the ligand functionality. Thus, the direct, facile low-temperature formation of $Zn_4O\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_6$[2] and the fast, clean exchange of $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ for acetate in $Mo_2(MeCOO)_4$[3] were unforeseen but can be explained

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[1] Meng, X.; Rath, N. P.; Fehlner, T. P.; Rheingold, A. L. *Organometallics* **1991**, *10*, 1986.

[2] Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1991**, *30*, 3120.

[3] Cen, W.; Lindenfeld, P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5451.