difference may be attributed to the increase in the charge density over the iron centers. This increase is brought about by the electron-donating effects induced by the methyl groups on the bridging and the C_5Me_5 ligands. The same behavior has been observed in the *p*-phenylene-bridged biferrocenes (η^5-C_5Me_5)Fe(η^5-C_5Me_4-*p*-C_6H_4-η^5-C_5Me_4)Fe(η^5-C_5Me_5) and (η^5-C_5H_5)Fe(η^5-C_5Me_4-*p*-C_6H_4-η^5-C_5Me_4)Fe(η^5-C_5H_5) where the first oxidation occurs at 0.084 and 0.276 V, respectively.[19] Methyl substitution seems to affect noticeably the first oxidation potential; however, the second oxidation occurs at nearly identical potentials.

The synthesis of the mono- and dioxidized species, derived from **4a** and **4b**, and the study of their spectroscopic and magnetic properties are presently under way and will be reported in a future paper.

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Registry No. 2, 112713-01-6; 3, 112713-02-7; 4a, 112713-03-8; 4b, 112713-04-9; (η^5-C_5Me_2)Fe(acac), 97210-26-9; (η^5-C_5Me_5)Ni(acac), 97210-29-2; bis(trimethylsilyl)acetylene, 14630-40-1; 3,4-dimethylcyclopent-2-en-1-one, 30434-64-1.

Supplementary Material Available: Tables of data collection and structure solution details, atomic positional parameters, thermal parameters, root-mean-square amplitudes of vibration, and bond distances and angles for **4b** (7 pages); a listing of $10|F_o|$ vs. $10|F_c|$ for **4b** (6 pages). Ordering information is given on any current masthead page.

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[19] Bunel, E. E.; Campos, P.; Ruz, J.; Valle, L.; Chadwick, I.; Santa Ana, M.; Gonzalez, G.; Manriquez, J. M. *Organometallics*, in press.

Synthesis of [$Pd_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] and Its Reaction with Acids. Structure of [$Pd_3(\eta^5$-$C_5Me_5)_3(\mu_3$-$CO)_2]^+[CF_3SO_3]^-$

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Summary: The complex [$Pd_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] (**1**) has been synthesized by the reaction of [$PdCl(CO)]_n$ with $C_5Me_5MgCl\cdot THF$. The dimer **1** reacts with HBF_4 or CF_3SO_3H to give [$Pd_3(\eta^5$-$C_5Me_5)_3(\mu_3$-$CO)_2]^+$ whose structure as the $CF_3SO_3^-$ salt was solved by X-ray crystallography.

Nickel and platinum complexes of the type [$M_2(\eta^5$-$C_5R_5)_2(CO)_2$] have been observed when R is H or an alkyl group.[2,3] However, the corresponding palladium system has only been described when R = Ph.[4] Dimeric palladium complexes containing the stabilizing pentaphenylcyclopentadienyl group are not unusual, but they are primarily associated with alkyne oligomerization.[4] Similar palladium species containing η^5-C_5R_5 (R = H, Me) are far rarer. We have devised a synthesis of the pentamethylcyclopentadienyl dimer [$Pd_2(\eta^5$-$C_5Me_5)_2(\mu_2$-$CO)_2$] (**1**) and are investigating the chemistry associated with the metal–metal bond and the Pd(η^5-C_5Me_5)(CO) molecular fragment. Herein, we describe the synthesis of **1** and its unusual reactivity with acids.

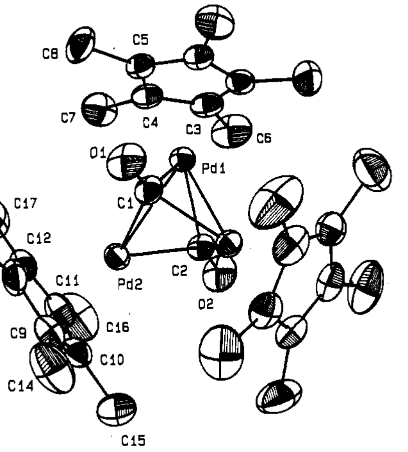

Figure 1. ORTEP drawing of [$Pd_3(\eta^5$-$C_5Me_5)_3(\mu_3$-$CO)_2]^+$ (**2b**) with non-hydrogen atoms represented by thermal ellipsoids at the 50% probability level: Pd_1–Pd_2, 2.6254 (3) Å; Pd_2–$Pd_{2'}$, 2.6207 (4) Å; Pd_1–C_1, 2.171 (4) Å; Pd_1–C_2, 2.033 (4) Å; Pd_2–C_1, 2.061 (3) Å; Pd_2–C_2, 2.134 (3) Å; Pd_1–C_{g1} (center of gravity of Cp*), 1.926 Å; Pd_2–C_{g2} (center of gravity of Cp*), 1.939 Å; Pd_2–Pd_1–$Pd_{2'}$, 59.88 (1)°; Pd_1–Pd_2–$Pd_{2'}$, 60.059 (5)°.

Treatment at −30 °C of a THF slurry of the palladium(I) polymer [$PdCl(CO)]_n$ with $C_5Me_5MgCl\cdot THF$ affords purple, temperature-sensitive crystals of [$Pd_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] (**1**) in 44% yield.[5,6] This method contrasts with the synthesis of the pentaphenylcyclopentadienyl analogue which was prepared by reduction under CO of a Pd(II) precursor.[4]

The presence of a single band at 1839 cm^{-1} in the IR spectrum of hexane solutions of **1** indicates that the carbonyl groups bridge the two palladium atoms and that the carbon–oxygen vectors are coplanar. This contrasts with the related nickel complexes [$Ni_2(\eta^5$-$C_5R_5)_2(\mu$-$CO)_2$] (R = H, Me), which, with one exception (C_5R_5 = C_5H_4Me), have a puckered central core and exhibit symmetric and asymmetric carbonyl absorption bands in their solution IR spectra,[7,8] and with the platinum complexes [$Pt_2(\eta^5$-

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[2] Boag, N. M. *Organometallics*, in press.

[3] Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 6.

[4] Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.

[5] [$PdCl(CO)]_n$ may be prepared by treatment of [$PdCl_2$] with CO (5 atm) in acetic anhydride: Goggin, P. L.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1974**, 534. Belli Dell'Amico, D.; Calderazzo, F.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 137. $C_5Me_5MgCl\cdot THF$ has been described: Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.

[6] In a typical reaction, a suspension of [$PdCl(CO)]_n$ (1.0 g, 5.9 mmol) in THF (70 mL) at −25 °C was treated with a THF solution of $C_5Me_5MgCl\cdot THF$ (14.1 mL of a 0.418 M solution). The solution was stirred for 2 h at −25 °C and then stripped to dryness in vacuo at the same temperature. The residue was extracted with prechilled hexane (500 mL) at 0 °C and filtered rapidly through a Celite pad into a cooled vessel under dinitrogen. Cooling to −78 °C (2–3 days) afforded maroon crystals of [$Pd_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] (1) (0.696 g, 44%). Spectroscopic data for 1: IR (hexane) ν(CO) 1839 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) 1.87 ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, −40 °C) 218.7 (CO), 106.7 CMe), 9.6 (Me) ppm. Anal. Calcd for $C_{22}H_{20}O_2Pd_2$: Pd, 39.5. Found: Pd, 39.4, 38.9.

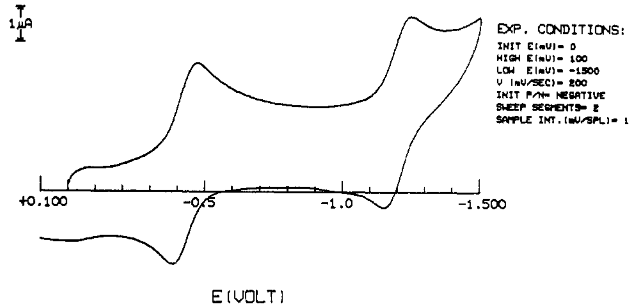

Figure 2. Cyclic voltammogram of complex **2b** measured in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate at a Pt working electrode using a scan rate of 200 mV s^{-1}. Reference is Ag/AgCl.

$C_5R_5)_2(CO)_2]$ (R = H, Me), which have terminal carbonyl groups.[2,9]

Treatment of ethereal solutions of 1 with either HBF_4 or CF_3SO_3H led to the precipitation of very dark metallic green microcrystals of $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^+X^-$ (**2a**, X = BF_4; **2b**, X = CF_3SO_3). Solutions of **2a** in nitromethane had conductivities associated with 1:1 electrolytes. Intense red solutions of **2** in dichloromethane exhibit a band at 1769 cm^{-1} in their IR spectra indicative of a triply bridging carbonyl group, and no metal hydride absorptions could be detected in the ^1H NMR spectrum.[10] This was an unexpected result since protonation of complexes of the type $[M_2(\eta^5\text{-}C_5R_5)_2(CO)_{2n}]$ generally affords the hydrido-bridged cations $[M_2(\mu\text{-}H)(\eta^5\text{-}C_5R_5)_2(CO)_{2n}]^+$.[11]

An X-ray structure of **2b** (Figure 1) revealed it to consist of an approximately equilateral triangle of palladium atoms (mean Pd–Pd = 2.63 Å) with each face capped with a triply bridging carbonyl group and the three corners capped by $\eta^5\text{-}C_5Me_5$ ligands.[12] The molecule is bisected by a crystallographic mirror plane that lies perpendicular to the plane defined by the triangle of palladium atoms, passes through C3 and C6 of the pentamethylcyclopentadienyl group, and contains Pd1 and the two carbonyl groups. This mirror plane also orthogonally bisects the sulfur–carbon bond of the counterion which as a consequence has disorder between the CF_3 and SO_3 groups.

This Pd_3^+ cluster belongs to the family of the Fischer–Palm and related molecules $[Ni_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}CO)_2]$ (R = H, Me; charge = 1+, 0, 1–) studied extensively by Dahl.[13] It represents the first isolated and structurally characterized example of a 48-valence-electron cluster of this particular type, although it may be compared to other 48e clusters such as $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$.[14]

Cyclic voltammograms of **2** reveal two discrete redox processes (Figure 2). A reversible reduction is encountered at –0.43 V vs. Ag/AgCl and a second less reversible reduction at –1.22 V.

These data may imply facile electrochemical interconversions to the 49- and 50-valence-electron clusters. The partial reversibility of the second reduction wave could also indicate that the putative anion $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^-$ is less stable at room temperature than its nickel analogue. This is not an unexpected result since the poorer back-bonding ability of carbonyl groups on palladium compared to nickel would destabilize the electron-rich palladium cluster relative to its nickel counterpart.[15]

The isolation of 1 and its unusual reactivity with acids presage a rich and diverse chemistry for the (pentamethylcyclopentadienyl)palladium system. Preliminary studies of 1 indicate that carbonyl groups are readily lost from the palladium leading to unsaturation and cluster formation. We will describe these results in due course.

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Supplementary Material Available: Tables of experimental details, atomic coordinates, thermal parameters, and bond lengths and angles (12 pages); a listing of structure factors (32 pages). Ordering information is given on any current masthead page.

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(7) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391.

(8) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 680.

(9) Fischer, E. O.; Schuster-Woldan, H.; Bittler, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1963**, *18B*, 429. Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585.

(10) Spectroscopic data for 2: IR (CH_2Cl_2) ν(CO) 1769 cm^{-1}; ^1H NMR (CD_2Cl_2, 500 MHz, –70 °C) 1.78 ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz, –70 °C) 211.4 (CO), 113.2 (CMe), 9.3 (Me) ppm; conductivity data, Λ_m (nitromethane, 1.08 mM solution) 97.6 Ω^{-1} cm^2 mol^{-1}.

(11) Davidson, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653.

(12) Crystal data: formula $C_{33}H_{45}F_3O_5Pd_3S$, monoclinic, $P2_1/m$, Z = 2, a = 8.440 (2) Å, b = 20.867 (5) Å, c = 10.806 (2) Å, β = 108.81 (2)°; data were collected by using the ω–2θ scan technique up to a maximum 2θ of 52°; total reflections = 4656 of which 3645 were unique; reflections with $I > 3\sigma(I)$ = 3112; solved by direct methods; refined by full-matrix least squares; R = 0.032, R_w = 0.051.

(13) Fischer, E. O.; Palm, C., *Chem. Ber.* **1958**, *91*, 1725. Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054.

(14) Olson, W. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7657.

(15) Belli Dell'Amico, D.; Calderazzo, F.; Veracini, C. A.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 3030. Majima, T.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *134*, C45.

Fluxionality of Phosphine and Phosphite Ligands on a Coordinatively Unsaturated Platinum Cluster Complex

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Summary: The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) adds phosphine or phosphite ligands (L) to give $[Pt_3(\mu_3\text{-}CO)L(\mu\text{-dppm})_3]^{2+}$, which exhibit fluxional behavior involving migration of the ligand L around the triangular face of the cluster. This is the first time that such fluxionality involving phosphorus donor ligands has been observed, and the ease of reaction is attributed to the coordinative unsaturation of the clusters.

Phosphorus donor ligands are of major importance in metal cluster chemistry, but there are no known examples of easy migration of such ligands between metal centers; even phosphine ligand migration between coordination sites on the same metal atom is rare.[1-5] We are therefore

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(1) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403.

(2) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1037.

(3) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

(4) Farrar, D. H.; Lunniss, J. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1249.

(5) Shaffer, M. R.; Keister, J. B. *Organometallics* **1986**, *5*, 561.

0276-7333/88/2307-0792$01.50/0