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Supplementary Material Available: ORTEP drawing of 1 and tables of crystal data, fractional atomic coordinates, isotropic or equivalent thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond lengths and angles for 1 and 2 (13 pages). Ordering information is given on any current masthead page.

Synthesis of Novel Diplatinum Complexes Containing the (Diphenylphosphino)cyclopentadienyl Ligand

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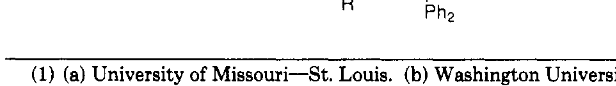
Summary: The reactions of [PtClR(cod)] with $TlC_5H_4PPh_2$ yield the novel dimeric complexes $[Pt_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1a**, R = Me; **1b**, R = Ph). The structure of **1b** has been determined by X-ray diffraction, and the molecule does not possess the expected center of symmetry. This lack of a symmetry element persists in solution at low temperatures for both compounds. Treatment of **1a** with carbon monoxide yields the face-to-face dimer $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**), in which an η^5 to η^1 rearrangement of the cyclopentadienyl group has occurred. Reaction of **1a** or **1b** with CNBu^t yields $[PtR(CNBu^t)_2(Ph_2PC_5H_4)]$, in which the C_5H_4 unit is uncoordinated. The intermediate $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ has been characterized spectroscopically.

The (diphenylphosphino)cyclopentadienyl ligand (dppc) has been used as a heterodifunctional ligand in the construction of both homo- and heteronuclear dimetallic compounds.[2-6] We have recently employed dppc, and the related dicyclopentadienylphenylphosphine group, in the preparation of mixed-metal species containing zirconium and platinum.[7] We report here our preliminary results involving the use of dppc in the synthesis of novel organoplatinum dimers.

When a benzene solution of [PtClR(cod)] (R = Me, Ph; cod = 1,5-cyclooctadiene) is allowed to react with 1 mol equiv of $TlC_5H_4PPh_2$[2] at 25 °C under an argon atmosphere, a precipitate of thallium chloride is formed. After filtration through a short alumina column, concentration of the solution and addition of petroleum ether provides $[Pt_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1a**, R = Me; **1b**, R = Ph) as a yellow solid in up to 80% yield (eq 1). Complexes **1a** and **1b** have been characterized by their ^1H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra, and the structure of **1b** has been determined by single-crystal X-ray crystallography (Figure 1).[8]



$$2[PtClR(cod)] + 2TlC_5H_4PPh_2 \longrightarrow [Pt_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2] + 2TlCl \quad (1)$$

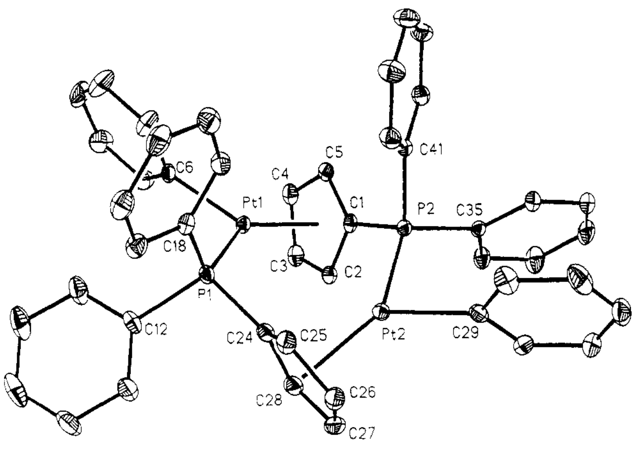


Figure 1. ORTEP drawing of $[Pt_2Ph_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1b**), showing the atom labeling scheme. Selected bond distances (Å) and angles (deg) include the following: Pt1–P1 = 2.198 (1), Pt2–P2 = 2.200 (2), Pt1–C1 = 2.350 (3), Pt1–C2 = 2.392 (3), Pt1–C3 = 2.446 (4), Pt1–C4 = 2.303 (4), Pt1–C5 = 2.335 (4), Pt2–C24 = 2.380 (4), Pt2–C25 = 2.370 (4), Pt2–C26 = 2.308 (6), Pt2–C27 = 2.445 (5), Pt2–C28 = 2.474 (5), P1–C24 = 1.808 (5), P2–C1 = 1.803 (4), Pt1–C6 = 2.025 (4), Pt2–C29 = 2.018 (4), P1–C12 = 1.832 (5), P1–C18 = 1.818 (4), P2–C35 = 1.829 (3), P2–C41 = 1.825 (4); P1–Pt1–C6 = 96.8 (1), P2–Pt2–C29 = 87.0 (2), Pt1–P1–C24 = 112.4 (1), Pt2–P2–C1 = 111.0 (1).

Table I. NMR Spectroscopic Parameters for $[Pt_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)]$[a]

	1a (R = Me)	**1b** (R = Ph)
	^1H NMR	
CH_3 H_A	0.30 (d, $^3J_{PH}$ = 1.8, $^2J_{PtH}$ = 91.4)	
H_B	0.88 (d, $^3J_{PH}$ = 2.3, $^2J_{PtH}$ = 88.3)	
C_5H_4 (A)	4.61, 4.85, 6.32, 6.49	4.63, 5.05, 6.02, 6.42
(B)	5.71, 6.39, 6.42, 6.77	5.58, 6.14, 6.20, 6.54
	$^{13}C\{^1H\}$ NMR	
CH_3 C_A	−36.5 ($^1J_{PtC}$ = 800)	
C_B	−2.8 ($^1J_{PtC}$ = 870)	
	$^{31}P\{^1H\}$ NMR	
P_A	16.8 (d, J_{PP} = 20, J_{PtP} = 3969, 126)	12.7 (d, J_{PP} = 22, J_{PtP} = 3589[b])
P_B	−13.3 (d, J_{PP} = 20, J_{PtP} = 4147, 305)	−21.0 (d, J_{PP} = 22, J_{PtP} = 4085, 351)
	$^{195}Pt\{^1H\}$ NMR	
Pt_A	−3389 (dd, J_{PtP} = 3961, 311, J_{PtPt} = 1134)	−3045 (dd, J_{PtP} = 3587, 345, J_{PtPt} = 1100)
Pt_B	−4278 (dd, J_{PtP} = 4152, 110, J_{PtPt} = 1134)	−4103 (br d, J_{PtP} = 4073,[b] J_{PtPt} = 1100)

[a] Chemical shifts are in ppm relative to Me_4Si (^1H, ^{13}C), H_3PO_4 (^3P), or K_2PtCl_4 (^{195}Pt), positive shifts representing deshielding. Coupling constants are in hertz. [b] The second J_{PtP} value is unresolved.

The molecular structure of **1b** reveals a dimeric framework in which the dppc ligands are bound in a "head-to-tail" fashion. The molecule does not possess the expected

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(8) Crystal data for **1b**: $C_{46}H_{38}P_2Pt_2$; space group $P\bar{1}$; cell dimensions a = 10.256 (4) Å, b = 13.693 (5) Å, c = 14.687 (7) Å, α = 95.52 (3)°, β = 109.68 (3)°, γ = 101.87 (3)°; Z = 2; V = 1869.7 (13) Å^3; d(calcd) = 1.852 Mg/m^3. The 9404 measured reflections were collected with use of a 2θ–θ scanning technique and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by using the SHELXTL PLUS program. All non-hydrogen atoms were located and refined anisotropically. Hydrogen atom positions were calculated and were refined isotropically with use of the Riding model. Refinement with the 6759 unique observed reflections with $F > 6.0\sigma(F)$ converged at R = 0.0221 and R_w = 0.0266.

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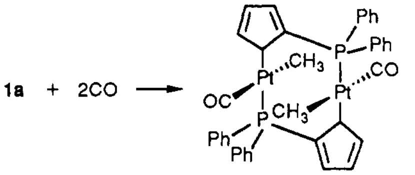
center of symmetry, however, in contrast to the related complex $[Rh_2(CO)_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$.[6] If the two Pt atoms, the two P atoms, and the centroids of the two cyclopentadienyl rings are considered to form a six-membered ring, the molecule may be said to adopt a distorted-boat conformation. The distortion is such that the two P–Pt–Ph angles differ by 10°, for example. This unsymmetrical structure persists in solution at low temperature for both **1a** and **1b**, as evidenced by multinuclear magnetic resonance measurements (Table I). Thus, for example, the $^{31}P\{^1H\}$ NMR spectrum of **1a** at −55 °C consists of two doublets, each exhibiting both short- and long-range coupling to ^{195}Pt. Warming to 25 °C results in broadening of these signals, followed by coalescence, and heating to 100 °C produces a single, very broad resonance; decomposition occurs above this temperature, so a fast-exchange limiting spectrum is not obtained. Similar results are obtained for solutions of **1b**.

When a CH_2Cl_2 solution of **1a** is treated with carbon monoxide (1 atm) at ambient temperature, the 16-electron complex $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**) is obtained as a yellow solid in 90% yield (eq 2). Coordination of CO is accompanied by an η^5 to η^1 rearrangement of the cyclopentadienyl moiety,[9] and the face-to-face square-planar complex exists as that isomer in which the carbonyl and methyl groups lie mutually trans to one another.[10] This reaction is unusual in that an 18-electron complex gains a CO ligand but simultaneously becomes coordinatively unsaturated. In contrast to the case for **1a**, the NMR spectra of **2a** exhibit single methyl, carbonyl, and phosphorus resonances. The analogous reaction of **1b** produces an insoluble solid.[11]



(2)

Addition of 6–10 equiv of $CNBu^t$ to a CH_2Cl_2 solution of **1a** or **1b** results in cleavage of the Pt–Cp linkages and generation of a monomeric complex of the form *trans*-$[PtR(CNBu^t)_2(Ph_2PC_5H_4)]$ (**3a**, R = Me; **3b**, R = Ph).[12] The $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** exhibit $^1J_{PtP}$ values around 1500 Hz, consistent with the P atom lying trans to R,[13] and the ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit only two and three signals, respectively, for the C_5H_4 group, which suggests that the cyclopentadienyl group is uncoordinated. We formulate the complexes as zwitterions, having a formal positive charge on platinum and a negative charge associated with the cyclopentadienyl ring. Complex **3a** and the isonitrile analogue of **2a**, namely $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$, are in dynamic equilibrium in solution, **2a** being favored in the absence of excess isonitrile. Thus, when a benzene solution of **1a** is treated with 2 mol equiv of $CNBu^t$ (1 mol equiv per Pt) $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ is formed in near-quantitative yield, as evidenced by NMR spectroscopy.[14]

Complexes **1** and **2** represent suitable substrates for studying dinuclear elimination reactions from complexes in which the organic fragments are constrained in one molecule but are attached to different metal centers, and these and related reactions will be discussed elsewhere.

Acknowledgment. Financial support from the University of Missouri—St. Louis is gratefully acknowledged. M.L. thanks Mallinckrodt Inc. for a graduate fellowship.

Supplementary Material Available: $^{31}P\{^1H\}$ NMR spectrum of **1a** in $CDCl_3$ solution at −55 °C and tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (10 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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(9) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.

(10) NMR data (δ) for **2a**·$0.6CH_2Cl_2$ in $CDCl_3$ solution: ^1H NMR CH_3 0.65 (d, $^3J_{PH}$ = 7 Hz, $^2J_{PtH}$ = 63 Hz), C_5H_4 4.90 (d, $^3J_{PH}$ = 13 Hz, $^2J_{PtH}$ = 148 Hz), 6.28 (m), 6.60 (m), and 7.40 (m), CH_2Cl_2 5.32 (0.6 molecules per dimer by integration); $^{13}C\{^1H\}$ NMR CH_3 4.0 (d, $^2J_{PC}$ = 7 Hz, $^1J_{PtC}$ = 564 Hz), C_5H_4 60.5 (dd, $^2J_{PC}$ = 57 Hz, 22 Hz), 120.5 (d, J_{PC} = 13 Hz), 134.4 (d, J_{PC} = 10 Hz), and 145.2 (d, J_{PC} = 12 Hz), C attached to P not observed, CO 180.3 (d, $^2J_{PC}$ = 6 Hz, $^1J_{PtC}$ = 1103 Hz); $^{31}P\{^1H\}$ NMR 12.5 ($^1J_{PtP}$ = 2659 Hz). Anal. Calcd for $C_{38.6}H_{35.2}Cl_{1.2}O_2P_2Pt_2$: C, 45.20; H, 3.46. Found: C, 45.01; H, 3.56. IR (ν(CO), KBr pellet): 2050 cm^{-1}.

(11) The IR spectrum of this solid exhibits a band at 2056 cm^{-1} due to ν(CO). The compound may be the phenyl analogue of **2a** or an oligomeric form.

(12) Selected NMR data (δ, $CDCl_3$ solution) for **3a**: ^1H NMR CH_3 0.65 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 58 Hz), $C(CH_3)_3$ 1.10 (s), C_5H_4 6.32 (s) and 6.34 (s); $^{13}C\{^1H\}$ NMR CH_3 −12.5 (d, $^2J_{PC}$ = 70 Hz, $^1J_{PtC}$ = 391 Hz), $C(CH_3)_3$ 29.5 (s), $C(CH_3)_3$ 58.2 (s), C_5H_4 92.3 (d, J_{PC} = 74 Hz), 110.0 (d, J_{PC} = 15 Hz), and 116.0 (d, J_{PC} = 17 Hz); $^{31}P\{^1H\}$ NMR 2.5 ($^1J_{PtP}$ = 1568 Hz). **3a** loses $CNBu^t$ on attempted isolation and so has not been obtained as an analytically pure material. Selected NMR data (δ, $CDCl_3$ solution) for **3b**: ^1H NMR $C(CH_3)_3$ 1.10 (s), C_5H_4 6.40 (m) and 6.47 (m); $^{13}C\{^1H\}$ NMR $C(CH_3)_3$ 29.1 (s), $C(CH_3)_3$ 58.4 (s), C_5H_4 90.5 (d, J_{PC} = 74 Hz), 110.4 (d, J_{PC} = 16 Hz), and 116.3 (d, J_{PC} = 17 Hz); $^{31}P\{^1H\}$ NMR −2.1 ($^1J_{PtP}$ = 1484 Hz). Anal. Calcd for $C_{33}H_{37}N_2PPt$: C, 57.64; H, 5.38; N, 4.07. Found: C, 57.17; H, 5.38; N, 4.40.

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(14) Selected NMR data (δ) for $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ ($CDCl_3$ solution): ^1H NMR CH_3 0.50 (d, $^3J_{PH}$ = 6 Hz, $^2J_{PtH}$ = 62 Hz), $C(CH_3)_3$ 0.88 (s), C_5H_4 5.18 (d, $^3J_{PH}$ = 12 Hz, $^2J_{PtH}$ = 141 Hz), 6.22 (m), and 6.40 (m) (remaining signal obscured); $^{13}C\{^1H\}$ NMR CH_3 −1.0 (d, $^2J_{PC}$ = 7 Hz, $^1J_{PtC}$ = 541 Hz), $C(CH_3)_3$ 29.6 (s, $^3J_{PtC}$ = 32 Hz), $C(CH_3)_3$ 54.6 (s, $^1J_{PtC}$ not observed); $^{31}P\{^1H\}$ NMR 12.6 ($^1J_{PtP}$ = 3028 Hz).

Preparation and Chemical Reactivities of the Tungsten Allenyl Complex $CpW(CO)_3CH{=}C{=}CH_2$

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Summary: The tungsten propargyl complex $CpW(CO)_3CH_2C{\equiv}CH$ (**1**; Cp = η^5 C_5H_5) readily converts to the η^1-allenyl complex $CpW(CO)_3CH{=}C{=}CH_2$ (**2**) when dissolved in benzene or heated in CH_3CN. A rough estimation of the energy of activation for such a process possibly indicates 1,3-tungsten sigmatropic rearrangement. The reaction of tetracyanoethylene with **1** or **2** occurs readily in both cases to give the complex $CpW(CO)_3C_5H_3(CN)_4$ (**3**) with a cyclopentene ring bonded to W in a η^1 fashion. At 70 °C, complex **2** reacts with $Fe_2(CO)_8(\mu\text{-}CH_2)$ to produce a tungsten-substituted trimethylenemethane iron carbonyl complex, $CpW(CO)_3(\mu\text{-}\eta^4\text{-}C_4H_5)Fe(CO)_3$ (**4**). The structure assignment of complex **4** is based on spectroscopic data.

The chemistry of organometallic complexes containing one or more M–C σ bonds has long been a subject of interest.[1] However, due to its rarity, chemical reactivities

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