are valuable precursors to a variety of cyclic compounds, including iodolactones[10] and α,β-unsaturated γ-lactones.[12]

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

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(12) King, G. S.; Wright, E. S. *J. Chem. Soc., Perkin Trans. 1* 1974, 1499.

Organotransition-Metal Complexes of Multidentate Ligands. 11. Synthesis, Structure, and Reactivity of the First Intramolecular Coordination Compound with a Weakly Bound η^2-Arene[1]

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Summary: Thermolysis of $(PhHCPz'_2)Mo(CO)_4$ (**1**) in DME gives $(PhHCPz'_2)Mo(CO)_3$ (**2**) (Pz' = 3,5-dimethylpyrazol-1-yl); comparison of the structural details of the two compounds and the reactivity of **2** show that this compound is the first example containing an intramolecularly coordinated η^2-arene ligand.

Though the intramolecular η^2-bound arenes of transition metals were proposed 19 years ago as plausible intermediates prior to the activation of the aromatic carbon–hydrogen bonds, which is often referred to as "ortho metalation",[2] all the reports concerning the activation available today center on the intermolecular η^2-bound ligands.[3] If difficulty in isolating the intermediates can be attributed to the facile formation of a nearly unstrained four- or five-membered ring through the proximity effect,[4] suitable adjustments may bring an electrophilic center close sterically to one π-bond of a more distant phenyl fragment so that the internal η^2-arene intermediates can be isolated by virtue of the high kinetic or thermodynamic energy barrier which may be required for converting the intermediates into the unfavorable six-or-more-membered ortho metalated complexes (Scheme I). Since the electron-deficient compound $(H_2CPz'_2)Mo(CO)_3$ (Pz' = 3,5-dimethylpyrazol-1-yl) is apparently involved as an intermediate in the formation of the product compound $[(H_2CPz'_2)Mo(CO)_3]_2$, obtained from thermolysis of $(H_2CPz'_2)Mo(CO)_4$,[1c] this recognition has prompted us to attempt to isolate the intermediates using the bulkier bidentate ligands RR'CPz'₂ with R = R' = arene. We hope that the larger ligand would impede dimerization of the intermediates and increase the probability of a bonding interaction between one π-bond of an arene in RR'CPz'₂ and the electron-deficient metal center. Here we wish to report our preliminary results showing that the first intramolecular coordination compound with a weakly bound η^2-arene is indeed isolable by application of the strategy. We believe that it may have general applicability in the preparation of the intramolecular η^2-arene compounds, the probable precursors leading to the ortho metalated complexes. Furthermore, our results also imply that the intramolecular attachment of an η^2-arene can prevent the reported replacement of the binding arene by stronger nucleophiles in the $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$ complexes.[3b]

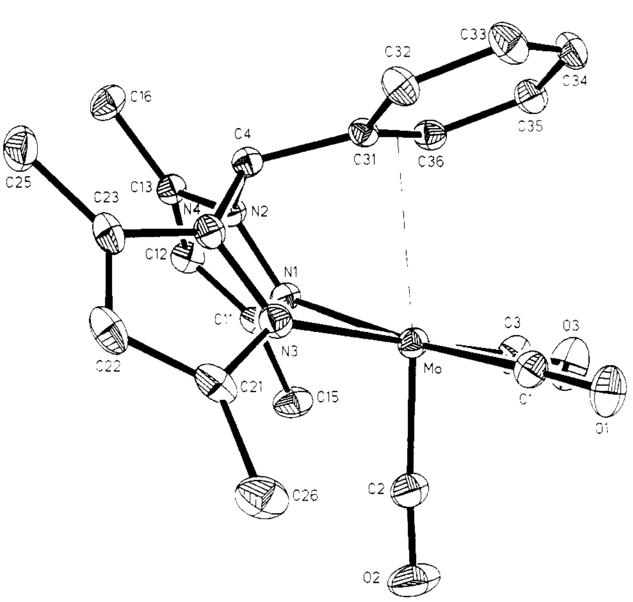

Figure 1. Structure of $(PhHCPz'_2)Mo(CO)_3$ (**2**) illustrating the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) are as follows: Mo–C(1), 1.941 (4); Mo–C(2), 1.897 (5); Mo–C(3), 1.928 (5); Mo–N(1), 2.292 (3); Mo–N(3), 2.265 (3); C(31)–C(32), 1.394 (6); C(32)–C(33), 1.377 (6); C(33)–C(34), 1.378 (7); C(34)–C(35), 1.360 (6); C(35)–C(36), 1.395 (6); C(36)–C(31), 1.402 (6); Mo$\cdots$C(31), 2.766 (4); Mo$\cdots$C(36), 2.840 (4); $\angle$C(1)–Mo–C(3), 86.8 (2); $\angle$N(1)–Mo–N(3), 79.5 (1); $\angle$Mo–N(1)–N(2), 115.6 (2); $\angle$Mo–N(3)–N(4), 116.4 (2); $\angle$N(1)–N(2)–C(4), 117.0 (3); $\angle$N(3)–N(4)–C(4), 116.7 (3).

Thermolysis of $(PhHCPz'_2)Mo(CO)_4$ (1) in DME induced decarbonylation, giving $(PhHCPz'_2)Mo(CO)_3$ (2),[5]

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(1) (a) Part 1: Shiu, K.-B.; Vong, W.-J. *J. Chin. Chem. Soc. (Taipei)* 1987, *34*, 195. (b) Part 2: Shiu, K.-B.; Chang, C.-J. *Ibid.* 1987, *34*, 297. (c) Part 3: Shiu, K.-B.; Liou, K.-S. *Ibid.* 1988, *35*, 187. (d) Part 4: Shiu, K.-B.; Lee, L.-Y. *J. Organomet. Chem.* 1988, *348*, 357. (e) Part 5: Shiu, K.-B.; Chang, C.-J.; Wang, Y.; Cheng, M.-J. *J. Chin. Chem. Soc. (Taipei)* 1989, *36*, 25. (f) Part 6: Shiu, K.-B.; Lee, L.-Y. *Ibid.* 1989, *36*, 31. (g) Part 7: Shiu, K.-B.; Liou, K.-S.; Cheng, C. P.; Fang, B.-R.; Wang, Y.; Lee, G.-H.; Vong, W.-J. *Organometallics* 1989, *8*, 1219. (h) Part 8: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Cheng, C. P.; Wu. F.-J. *J. Organomet. Chem.* 1989, *359*, C1. (i) Part 9: Shiu, K.-B.; Shen, F.-M.; Wang, S.-L.; Wei, S.-C. *Ibid.* 1989, *372*, 251. (j) Part 10: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Wei, S.-C. *Organometallics*, in press.

(2) Parshall, G. W. *Acc. Chem. Res.* 1970, *3*, 139.

(3) (a) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* 1988, *110*, 5725 and references cited therein. (b) Harman, W. D.; Taube, H. *Ibid.* 1988, *110*, 7555.

(4) (a) Parshall, G. W. *Catalysis (London)* 1977, *1*, 335. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 73. (c) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* 1986, *86*, 451. (d) Omae, I. *J. Organomet. Chem. Libr.* 1986, *18*, 1; *Coord. Chem. Rev.* 1988, *83*, 137.

(5) (a) Preparation of 1: A solution containing $PhHCPz'_2$ (1.27 g, 4.55 mmol) and $Mo(CO)_6$ (1.18 g, 4.47 mmol) in DME (30 mL) was refluxed for 1.5 h. The solvent was then removed under vacuum. Recrystallization of the solid residue from CH_2Cl_2/hexane produced yellow-green blocks of 1 in typical yields of 85%. Anal. Calcd for $C_{21}H_{20}MoN_4O_4$: C, 51.64; H, 4.14; N, 11.47. Found: C, 51.66; H, 4.13; N, 11.52. ^1H NMR (23 °C, acetone-d_6, 100 MHz): δ 7.77 (s, 1 H), 7.35 (m, 3 H), 6.39 (m, 2 H), 6.32 (s, 2 H), 2.63 (s, 6 H), 2.54 (s, 6 H), ppm. IR (CH_2Cl_2): ν_{CO} 2016 (m), 1898 (s), 1868 (s), 1820 (s) cm^{-1}. IR (KBr): ν_{CO} 2016 (m), 1882 (s), 1860 (s), 1816 (s) cm^{-1}. (b) Preparation of 2: A solution of 1 (3.0 mmol) in DME (50 mL) was refluxed for 70 h, giving an orange-yellow suspension. The suspension was cooled and filtered and the residue washed with 5 mL of CH_2Cl_2 and dried, yielding 1.22 g (88%). Anal. Calcd for $C_{20}H_{20}MoN_4O_3$: C, 52.18; H, 4.38; N, 12.17. Found: C, 51.85; H, 4.43; N, 12.12. ^1H NMR (23 °C, CD_2Cl_2, 100 MHz): δ 7.53 (m, 3 H), 7.07 (s, 1 H), 6.56 (m, 2 H), 6.05 (s, 2 H), 2.45 (s, 12 H) ppm. IR (CH_2Cl_2): ν_{CO} 1918 (s), 1798 (vs) cm^{-1}. IR (KBr): ν_{CO} 1914 (s), 1802 (s), 1770 (s) cm^{-1}.

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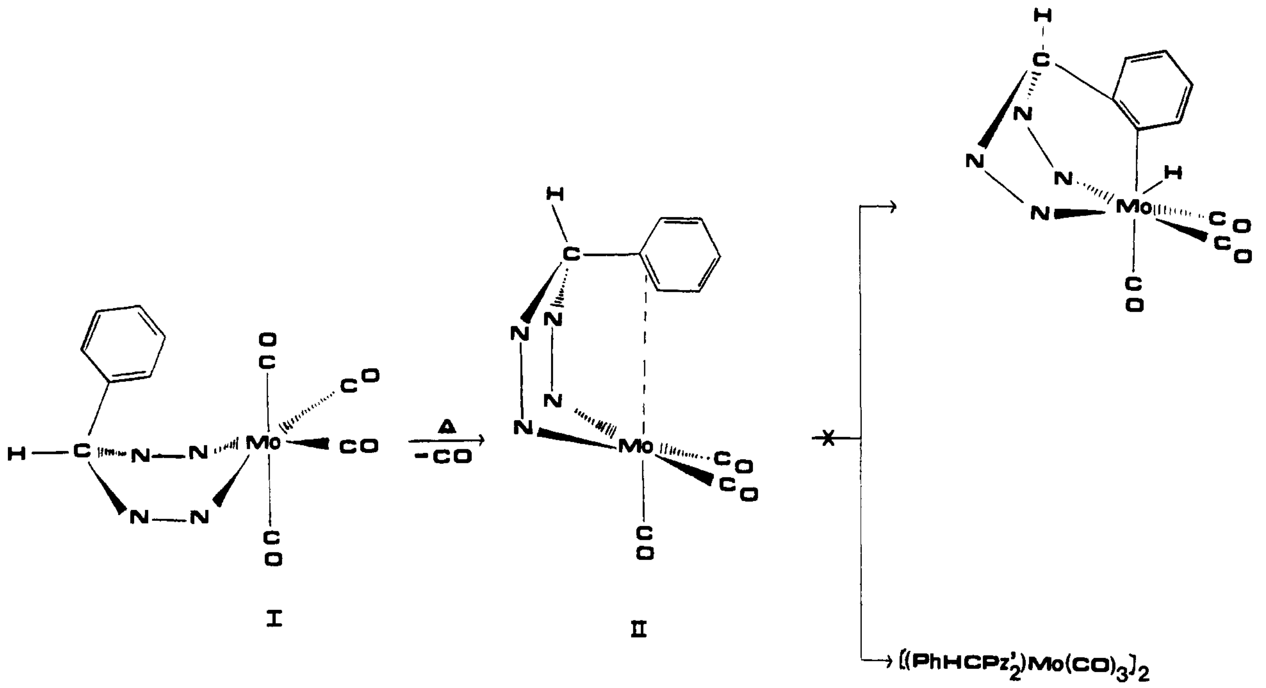
Scheme I



as shown in Scheme I. Both structural and chemical data for 1 and 2[6,7] strongly support that 2 is the compound with a weakly bound η^2-arene.

The molecular structures for 1 and 2 are depicted formally as I and II, respectively, in Scheme I; the ORTEP drawing of 2 is shown in Figure 1, while that of 1 is deposited as supplementary material. Thus, it is quite obvious that there is not any kind of bonding contact between the molybdenum atom and the phenyl fragment and all six C–C bond lengths of the fragment are not significantly different from the average value of 1.373 Å. However, this feature is only maintained for three such bonds, C(32)–C(33) (1.377 (6) Å), C(33)–C(34) (1.378 (7) Å), and C(34)–C(35) (1.360 (6) Å), in 2 (Figure 1). The other three bond lengths of 1.394 (6) Å for C(32)–C(31), 1.402 (6) Å for C(31)–C(36), and 1.395 (6) Å for C(36)–C(35) are significantly longer than 1.373 Å. Hence, it is likely that the perturbed phenyl ring is caused by some sort of bonding interaction present between the metal atom and the phenyl fragment in the formally electron-deficient compound 2. In fact, a comparison between interatomic distances, 2.766 Å for Mo···C(31), 2.840 Å for Mo···C(36), and 2.916 Å[8] for Mo···H(36), and the expected sum of the van der Waals radii,[9] ca. 3.6 Å for $Mo^0\cdots C(sp^2)$ and ca. 3.1 Å for $Mo^0\cdots H$, led us to believe that there does exist a weak bonding interaction[10] between the molybdenum atom and one olefinic bond of the phenyl fragment in 2. The η^2-bonded C(31)–C(36) is lengthened by 0.029 (6) Å. This value is much smaller than that (0.047 (6) Å) found in bis(tricyclohexylphosphine)(1,2-η^2-anthracene)nickel(0).[12b] Since the angles ∠Mo–N–N are 123.6 (2) and 125.0 (2)° for 1 and 115.6 (2) and 116.4 (2)° for 2 and the angles ∠N–N–C are 121.4 (3) and 121.3 (3)° for 1 and 117.0 (3) and 116.7 (3)° for 2, we believe that the more folded boat, $C(N\text{-}N)_2Mo$, in 2 relative to that in 1 increases the inherent ring strain, inhibiting any strong η^2-coordination (Scheme I).

The weak η^2-binding in 2 can find supporting evidence from the responses of 2 toward H_2 and $P(OMe)_3$:[7] (1) at room temperature or 50 °C, 2 resists oxidative addition of H_2, showing the coordinatively saturated nature[13] of the molybdenum atom in 2; (2) compound 2 reacts readily with $P(OMe)_3$ to give $(PhHCPz'_2)Mo(CO)_3[P(OMe)_3]$, indicating that the binding is not strong.

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully acknowledged.

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(6) (a) Crystal data for 1: a = 9.718 (2) Å, b = 14.198 (4) Å, c = 16.076 (4) Å, β = 96.62 (2)°, V = 2203 (1) Å^3, Z = 4, d_{calcd} = 1.472 g/cm^3 in space group $P2_1/n$. A total of 3198 unique intensities were collected by using Mo Kα radiation, 2° ≤ 2θ ≤ 50°, of which 2538 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals were R = 0.034 and R_w = 0.037. (b) Crystal data for 2: a = 9.582 (2) Å, b = 14.684 (6) Å, c = 14.224 (4) Å, β = 92.89 (2)°, V = 1999 (1) Å^3, Z = 4, d_{calcd} = 1.530 g/cm^3 in space group $P2_1/n$. A total of 3544 unique intensities were collected by using Mo Kα radiation, 2° ≤ 2θ ≤ 50°, of which 2532 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are R = 0.032 and R_w = 0.033.

(7) We added H_2 and $P(OMe)_3$ separately to the solution of 2 and obtained different results: (1) A stirred solution of 2 (0.46 g, 1.0 mmol) dissolved in 50 mL of CH_2Cl_2 was bubbled with H_2 at room temperature for 3 h. Since a solution IR spectrum indicated no sign of reaction, the solvent was removed and the resulting solid dissolved in 100 mL of THF. This solution was bubbled with H_2 in a 50 °C water bath for 3 h. A solution IR spectrum also showed no reaction. THF was then removed for recovery of 2 in ca. 99% yield. (2) To a stirred solution of 2 (1.0 mmol) dissolved in CH_2Cl_2 was added $P(OMe)_3$ (0.15 mL, 0.12 mmol). The solution soon changed from orange-yellow to pale yellow. After 15 min, 10 mL of hexane was added and CH_2Cl_2 was removed, giving milky yellow crystals. The crystals were collected, washed twice with 5 mL of hexane, and dried under vacuum to give 0.55 g (95%) of the product. Anal. Calcd for $C_{23}H_{29}MoPN_4O_6$: C, 47.26; H, 5.01; N, 9.59. Found: C, 46.92; H, 5.02; N, 9.42. ^1H NMR (23 °C, acetone-d_6, 100 MHz): δ 7.66 (s, 1 H), 7.27 (m, 3 H), 6.28 (s, 2 H), 6.10 (m, 2 H), 3.17 (d, 9 H, $^3J_{P,H}$ = 10.6 Hz), 2.61 (s, 6 H), 2.56 (s, 6 H) ppm. IR (CH_2Cl_2): ν_{CO} 1928 (s), 1818 (s), 1784 (s) cm^{-1}.

(8) This distance is a calculated value on the assumption of the ideal position of the hydrogen atom on a phenyl group at a C–H bond length of 0.96 Å. A longer distance of 2.966 Å is calculated at C–H = 0.92 Å.

(9) Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(10) The Mo^0–$C(sp^2)$ bonds typical of alkene are about 2.4 Å long.[11]

(11) (a) Connop, A. H.; Kennedy, F. G.; Knox, S. A. R.; Mills, R. M.; Ridging, G. H.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 518. (b) Cotton, F. A.; Frenz, B. A. *Acta Crystallogr.* **1974**, *30B*, 1772.

(12) Several η^2-arene complexes of d^{10} metals are known to have been characterized by X-ray crystallography. See: (a) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. (b) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1977**, *16*, 884. (c) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1978**, *B34*, 1849.

(13) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 85.

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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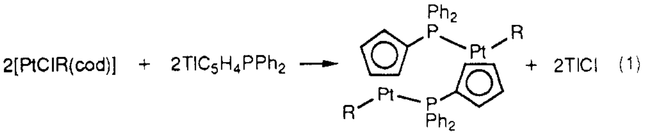
Summary: The reactions of [PtClR(cod)] with $TlC_5H_4PPh_2$ yield the novel dimeric complexes $[Pt_2R_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1a**, R = Me; **1b**, R = Ph). The structure of **1b** has been determined by X-ray diffraction, and the molecule does not possess the expected center of 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]



(1)

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

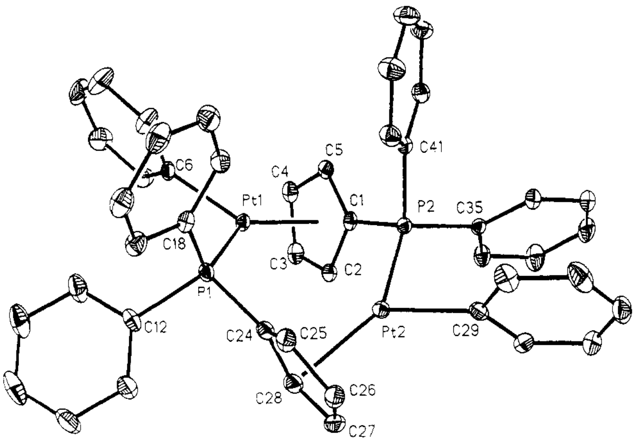


Figure 1. ORTEP drawing of $[Pt_2Ph_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)_2]$ (**1b**), showing the atom labeling scheme. Selected bond distances (Å) and angles (deg) include the following: Pt1–P1 = 2.198 (1), Pt2–P2 = 2.200 (2), Pt1–C1 = 2.350 (3), Pt1–C2 = 2.392 (3), Pt1–C3 = 2.446 (4), Pt1–C4 = 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 (^{3}P), or K_2PtCl_4 (^{195}Pt), positive shifts representing deshielding. Coupling constants are in hertz. [b] The second J_{PtP} value is unresolved.

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[1] (a) University of Missouri—St. Louis. (b) Washington University.

[2] Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1591-1596. Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574-7580. Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218-1220.

[3] Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882-3886.

[4] Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* **1986**, *5*, 888-894.

[5] DuBois, D. L.; Elgenbrot, C. W.; Miedaner, A.; Smart, J. C.; Haltiwanger, R. C. *Organometallics* **1986**, *5*, 1405-1411.

[6] He, X.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* **1987**, *6*, 678-680.

[7] Anderson, G. K.; Lin, M. *Organometallics* **1988**, *7*, 2285-2288.

[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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