# Synthesis and Reactivity of the Neutral Pyrazolate Complexes $[M_2\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-Rpz})_2]$ (M = Pd, Pt; Rpz = Pz, 3,5-dmpz, 4-Mepz) toward $AgClO_4$. Molecular Structure of $[Pt_2Ag\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-4-Mepz})_2]ClO_4$

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The neutral compounds $[Pt_2\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-Rpz})_2]$ (Rpz = pz (**2a**), 3,5-dmpz (**2b**), 4-Mepz (**2c**)) react with $AgClO_4$ in a 1:1 molar ratio to give the trinuclear compounds $[Pt_2Ag\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-Rpz})_2]ClO_4$ (Rpz = pz (**4a**), 3,5-dmpz (**4b**), 4-Mepz (**4c**)), which contain two Pt−Ag bonds. The reaction of $[Pd_2\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-3,5-dmpz})_2]$ (**3b**) with $AgClO_4$ renders $[\{Pd_2(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P)_2(\mu_3\text{-3,5-dmpz-}N,N',C^4)_2Ag(\eta^2\text{-}\mu_2\text{-}ClO_4)\}_2]$ (**5**), a palladium/silver compound with an unprecedented dmpz bridging ligand $\eta^1$-bonded to the Ag centers, a coordination mode involving only the $C^4$ atom of each dmpz ligand.

## Introduction

Metal−metal bonding in heteronuclear complexes containing $d^8$ and $d^{10}$ metal ions has been known for some years. A rich chemistry in this area has been developed in our group, involving the synthesis of heteronuclear $Pt^{II}$−M compounds[1−14] (M = Ag, Cu, Hg, Tl, Pb, Sn), which have usually been obtained by reacting mono- or dinuclear anionic pentahalophenyl complexes of $Pt^{II}$ with the corresponding complexes or salts of the metal M. In some cases the neutral mono- or dinuclear platinum complexes have been used for preparing Pt→M derivatives. However, complexes containing Pd→M bonds usually cannot be prepared, except for a few cases in which very long Pd−Ag bonds (if any) are supported by bridging ligands.[15−20] In the case of (perhalophenyl)palladate substrates, similar Pd−Ag derivatives have not been obtained mainly due to transarylation processes[2,4] or to a reluctance of the Pd center to engage in the formation of this type of Pd→M donor−acceptor bond.[5]

Recently we have described the synthesis of the neutral $M^{II}$ complexes [M(C∧P)(L∧L)] (M = Pt, Pd; C∧P = $CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P$; L∧L = $S_2CNMe_2$, $S_2COEt$, acac) and have studied their reactivity toward Hg(II)[21,22] and Ag(I)[23] salts. We have observed, when M = Pt, their ability to form heteronuclear compounds containing unsupported Pt−Hg donor−acceptor bonds when they react with Hg(II) salts ($HgX_2$, X = Br, I). However, the reactions of the analogous palladium complexes result in transmetalation (X = Br), giving rise to dinuclear compounds with the C∧P group acting as an unprecedented bridging ligand between the palladium and mercury atoms.

To explore further the possibilities of preparing Pd−Ag complexes, we have extended our work to the synthesis of new neutral dinuclear complexes of $Pd^{II}$ and $Pt^{II}$ containing the same C∧P group (C∧P = $CH_2C_6H_4P$-

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(*o*-tolyl)$_2$-κ*C*,*P*) and μ-azolato bridging ligands, [{M{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-Rpz)}$_2$] (M = Pt, Pd; Rpz = pyrazole (Hpz), 3,5-dimethylpyrazole (H3,5-dmpz), 4-methylpyrazole (H4-Mepz)), and have studied their reactivity toward Ag$^I$ species such as AgClO$_4$ and [Ag(OClO$_3$)(PPh$_3$)].

The results indicate the facility with which the platinum substrates form Pt−Ag bonds and the reluctance of Pd to form this type of bond. Some of the results presented in this paper have been communicated previously.[24]

## Experimental Section

**General Procedures.** Elemental analyses were performed on a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 200−4000 cm$^{-1}$). NMR spectra were recorded on either a Varian XL-200 or a Varian Unity 300 NMR spectrometer using the standard references.

**Safety Note.** *Caution!* Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

**Synthesis.** [{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-Cl)}$_2$],[25] [{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$],[26] and [{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-3,5-*dmpz*)}$_2$Ag]ClO$_4$[24] were prepared as described elsewhere.

**[{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (1a).** [{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-Cl)}$_2$] (0.859 g, 0.800 mmol) and AgClO$_4$ (0.332 g, 1.60 mmol) were suspended in THF (35 mL) and allowed to react for 4 h at room temperature in the dark. The AgCl that formed was filtered off through Celite and the resulting solution concentrated to ca. 3 mL. Methanol (20 mL) and KO$_2$CCH$_3$ (0.157 g, 1.60 mmol) were added, and the mixture was stirred for 15 min. The solid was filtered and recrystallized from CH$_2$Cl$_2$/*n*-pentane to give a yellow solid, **1a** (0.76 g, 85%). Anal. Found: C, 49.10; H, 4.25. Calcd for C$_{46}$H$_{46}$O$_4$P$_2$Pt$_2$: C, 49.55; H, 4.16. IR ($\nu_{max}$/cm$^{-1}$): $\nu_a$(COO) 1580 (vs). $^1$H NMR ([$^2$H]chloroform, 218 K): δ 2.01 (s, Me$_{acetate}$), 2.14 (s, Me$_{C\wedge P}$), 2.25 (d, $^2J_{HH}$ = 16.0 Hz, CH$_2$, 2H), 2.80 (d, $^2J_{HH}$ = 16.0 Hz, CH$_2$, 2H), 3.08 (s, Me$_{C\wedge P}$), 6.4−7.5 (m, C$_6$H$_4$).

**[{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-pz)}$_2$] (2a).** NEt$_3$ (2.5 mL) and Hpz (0.1364 g, 2.00 mmol) were added to a stirred suspension of [Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (**1a**; 0.5588 g, 0.50 mmol) in methanol (35 mL). The mixture was refluxed for 1 h, and after cooling, the white solid, **2a**, was filtered off and washed with methanol (0.5254 g, 92.7% yield). Anal. Found: C, 50.89; H, 4.18; N. 4.90. Calcd for C$_{48}$H$_{46}$N$_4$P$_2$Pt$_2$: C, 50.97; H, 4.10; N, 4.95. IR ($\nu_{max}$/cm$^{-1}$): 464 (s), 474 (s), 488 (m), 514 (w), 533 (s), 565 (s), 588 (s), 627 (m), 752 (m), 770 (w), 1054 (s), 1280 (s), 1588 (m). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 2.00 (s, Me$_{C\wedge P}$), 2.53 (s, Me$_{C\wedge P}$), 3.09 ($\nu_A$, $^2J_{HH}$ = 16.2 Hz, CH$_2$), 3.38 ($\nu_B$, $^2J_{HH}$ = 16.2 Hz, CH$_2$), 5.93 (s, H4), 6.3−7.8 (m, C$_6$H$_4$). MS (FAB+, CH$_2$Cl$_2$; *m*/*z*, %): 1130, 100% (M$^+$); 1063, 90% [(M − pz)$^+$].

**[{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-3,5-dmpz)}$_2$] (2b).** This compound was prepared similarly to **2a**: NEt$_3$ (4.5 mL), H3,5-dmpz (0.451 g, 4.69 mmol), [Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (**1a**; 1.7436 g, 1.564 mmol). Yield of **2b**: 1.4946 g, 80.5%. Anal. Found: C, 52.20; H, 4.95; N. 4.55. Calcd for C$_{52}$H$_{54}$N$_4$P$_2$Pt$_2$: C, 52.61; H, 4.58; N, 4.71. IR ($\nu_{max}$/cm$^{-1}$): 454 (s), 470 (s), 481 (w), 504 (w), 527 (s), 561 (m), 584 (s), 671 (m), 751 (s, sh), 1274 (m), 1565 (m). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 1.61 (s, Me$_{C\wedge P,\ 3,5-dmpz}$), 2.22 (s, Me$_{3,5-dmpz}$), 2.30 (d, $^2J_{HH}$ = 16.35 Hz, CH$_2$), 2.75 (s, Me$_{C\wedge P}$), 2.96 (d, CH$_2$), 5.58 (s, H$^4$), 6.2−7.5 (m, C$_6$H$_4$). MS (FAB$^+$, CH$_2$Cl$_2$; *m*/*z*, %): 1186, 85% (M$^+$); 1091, 100% [(M − 3,5-dmpz) $^+$].

**[{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-4-Mepz)}$_2$] (2c).** This compound was prepared similarly to **2a**: NEt$_3$ (2.5 mL), H4-Mepz (0.1968 g, 2.396 mmol), [{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (**1a**; 0.668 g, 0.599 mmol). Yield of **2c**: 0.5762 g, 83%. Anal. Found: C, 51.96; H, 4.29; N. 4.90. Calcd for C$_{50}$H$_{50}$N$_4$P$_2$Pt$_2$: C, 51.81; H, 4.35; N, 4.83. IR ($\nu_{max}$/cm$^{-1}$): 465 (m), 476 (m), 485 (m), 531 (m), 565 (m), 588 (m), 629 (m), 747 (s, sh), 818 (m, sh), 1074 (s), 1590 (m). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 1.81 (s, Me$_{4-Mepz}$), 2.08 (s, Me$_{C\wedge P}$), 2.54 (s, Me$_{C\wedge P}$), 3.12 ($\nu_A$, $^2J_{PtH}$ = 46.15 Hz, $^2J_{HH}$ = 18.4 Hz, CH$_2$), 3.38 ($\nu_B$, $^2J_{PtH}$ = 46.15 Hz, $^2J_{HH}$ = 18.4 Hz, CH$_2$), 6.2−7.6 (m, C$_6$H$_4$). MS (FAB$^+$, CH$_2$Cl$_2$; *m*/*z*; %): 1157, 20% (M$^+$); 1077, 100% [(M − 4-Mepz)$^+$].

**[{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-pz)}$_2$] (3a).** This compound was prepared similarly to **2a**: NEt$_3$ (2.5 mL), Hpz (0.1298 g, 1.906 mmol), [{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (0.687 g, 0.733 mmol). Yield of **3a**: 0.635 g, 90.8%. Anal. Found: C, 60.38; H, 4.14; N. 5.93. Calcd for C$_{48}$H$_{46}$N$_4$P$_2$Pd$_2$: C, 60.45; H, 4.86; N, 5.87. IR ($\nu_{max}$/cm$^{-1}$): 459 (s), 467 (s), 483 (s), 510 (w), 528 (s), 560 (m), 585 (m), 629 (m), 670 (m), 750 (m), 1050 (m), 1280 (w), 1583 (m), 1592 (m). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 1.98 (s, Me$_{C\wedge P}$), 2.65 (s, Me$_{C\wedge P}$), 3.18 (AB, CH$_2$), 5.87 (s, H$^4$), 6.4−7.6 (m, H$^3$, H,$^5$ C$_6$H$_4$). MS (FAB$^+$, CH$_2$Cl$_2$; *m*/*z*; %): 887, 50% [(M − pz)$^+$].

**[{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-3,5-dmpz)}$_2$] (3b).** This compound was prepared similarly to **2a**: NEt$_3$ (2.5 mL), H3,5-dmpz (0.250 g, 2.60 mmol), [{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (0.813 g, 0.867 mmol). Yield of **3b**: 0.8494 g, 97%. Anal. Found: C, 61.53; H, 5.16; N, 5.18. Calcd for C$_{52}$H$_{54}$N$_4$P$_2$Pd$_2$: C, 61.85; H, 5.39; N, 5.50. IR ($\nu_{max}$/cm$^{-1}$): 457 (s), 476 (s), 487 (s), 509 (m), 531 (s), 565 (s), 588 (s), 672 (w), 747 (s), 755 (s), 775 (s), 1276 (s), 1586 (w). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 1.61 (s, Me$_{C\wedge P}$), 1.68 (s, Me$_{3,5-dmpz}$), 2.28 (s, CH$_2$), 2.32 (s, Me$_{3,5-dmpz}$), 2.83 (s, CH$_2$), 2.87 (s, Me$_{C\wedge P}$), 5.57 (s, H$^4$), 6.2−7.5 (m, C$_6$H$_4$,). MS (FAB$^+$, CH$_2$Cl$_2$; *m*/*z*; %): 915, 85% [(M − 3,5-dmpz)$^+$]. $^{13}$C NMR: δ 159.96 (d, $J_{CP}$ = 35.0 Hz, 1C), 147.19 (s, C$^3$(3,5-dmpz)), 145.69 (s, C$^5$(3,5-dmpz)), 142.99 (d, $J_{CP}$ = 11.0 Hz, 1C), 142.54(d, $J_{CP}$ = 15.2 Hz, 1C), 135.48 (d, $J_{CP}$ = 54.7 Hz, 1C), 133.75 (d, $J_{CP}$ = 10.2 Hz, 1C), 133.40 (s, 1C), 132.54 (s, 1C), 132.3−131.9 (m, 2C), 131.49 (d, $J_{CP}$ = 38.2 Hz, 1C), 130.46 (d, $J_{CP}$ = 13.3 Hz, 2C), 130.26 (s, 1C), 129.04 (d, $J_{CP}$ = 22.1 Hz, 1C), 128.2 (d, $J_{CP}$ = 53.8 Hz, 1C), 125.55 (m, 3C), 103.14 (d, $J_{CP}$ = 3.2 Hz, C$^4$ (3,5-dmpz)), 28.57 (s, CH$_2$), 22.34 (d, $^3J_{CP}$ = 13.8 Hz, Me$_{C\wedge P}$), 21.50 (d, $^3J_{CP}$ = 8.3 Hz, Me$_{C\wedge P}$), 14.33 (s, Me$_{3,5-dmpz}$), 12.61 (s, Me$_{3,5-dmpz}$).

**[{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-4-Mepz)}$_2$] (3c).** This compound was prepared similarly to **2a**: NEt$_3$ (2.5 mL), H4-Mepz (0.1364 g, 1.661 mmol), [{Pd{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-O$_2$CCH$_3$)}$_2$] (0.500 g, 0.533 mmol). Yield of **3c**: 0.4546 g, 87%. Anal. Found: C, 60.87; H, 5.44; N, 5.59. Calcd for C$_{50}$H$_{50}$N$_4$P$_2$Pd$_2$: C, 61.17; H, 5.13 N, 5.70. IR ($\nu_{max}$/cm$^{-1}$): 458 (m), 468 (m), 481 (m), 509 (m), 526 (m), 560 (m), 584 (w), 630 (m), 748 (s), 762 (s), 816 (s, sh), 1074 (s), 1585 (m). $^1$H NMR ([$^2$H]chloroform, 293 K): δ 1.78 (s, Me$_{4-Mepz}$), 2.09 (s, Me$_{C\wedge P}$), 2.64 (s, Me$_{C\wedge P}$), 3.15 ($\nu_A$, $^2J_{HH}$ = 15.0 Hz, CH$_2$), 3.23 ($\nu_B$, $^2J_{HH}$ = 15.0 Hz, CH$_2$), 6.2−7.5 (m, C$_6$H$_4$). MS (FAB$^+$, CH$_2$Cl$_2$; *m*/*z*; %): 901, 40% [(M − 4-Mepz)$^+$].

**[{Pt{CH$_2$-C$_6$H$_4$-P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-pz)}$_2$Ag]ClO$_4$ (4a).** AgClO$_4$ (0.037 g, 0.18 mmol) was added to a solution of [{Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-κ*C*,*P*}(μ-pz)}$_2$] (**2a**; 0.2 g, 0.18 mmol) in CH$_2$Cl$_2$/OEt$_2$ (20 mL/8 mL), and the mixture was stirred at room temperature for 40 min in the dark. Then, the solution was evaporated to dryness and OEt$_2$ (20 mL) and CH$_2$Cl$_2$ (2 mL) were added to the residue, giving rise to a pale yellow solid, **4a** (0.1926 g, 81% yield). Anal. Found: C, 42.77; H, 3.28; N. 3.94. Calcd for AgC$_{48}$ClH$_{46}$N$_4$O$_4$P$_2$Pt$_2$: C, 43.07; H, 3.46; N, 4.10. $\Lambda_M$ = 89 Ω$^{-1}$ cm$^2$ mol$^{-1}$ (10$^{-3}$ M, MeOH). IR ($\nu_{max}$/

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$cm^{-1}$): 462 (s), 477 (s), 506 (m), 528 (s), 565 (s), 588 (s), 623 (s), 750 (s), 763 (s), 775 (s), 1098 (vs), 1587 (w). $^1H$ NMR ([$^2H$]-chloroform, 293 K): $\delta$ 1.43 (s, $Me_{C\wedge P}$), 2.90 (s, $Me_{C\wedge P}$), 3.28 (d, $^2J_{HH} = 18$ Hz, $^2J_{PtH} = 85.8$ Hz, $CH_2$), 4.00, (d, $^2J_{HH} = 18$ Hz, $^2J_{PtH} =132$ Hz, $CH_2$), 6.34 (s, $H^4$), 6.2−8.0 (m, $C_6H_4$, $H^3$, $H^5$). MS ($FAB^+$, $CH_2Cl_2$; *m*/*z*; %): 1239, 100% ($M^+$).

**[{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-3,5-dmpz)}$_2$Ag]$ClO_4$ (4b).** $AgClO_4$ (0.0364 g, 0.175 mmol) was added to a solution of [{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-3,5-dmpz)}$_2$] (**3a**; 0.2037 g, 0.171 mmol) in $CH_2Cl_2/OEt_2$ (40 mL/8 mL). After 1 h of stirring at room temperature in the dark, the solution was evaporated to dryness and $CH_2Cl_2$ (10 mL) was added to the residue. The filtered solution was evaporated to ca. 2 mL, and the addition of $Et_2O$ (15 mL) gave compound **4b** as a pale yellow solid. Yield: 0.189 g, 79%. Anal. Found: C, 44.93; H, 3.54; N. 3.66. Calcd for $AgC_{52}ClH_{54}N_4O_4P_2Pt_2$: C, 44.79; H, 3.90; N, 4.02. $\Lambda_M = 30\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($10^{-3}$ M, 1,2-dichloroethane). IR ($\nu_{max}/cm^{-1}$): 458 (w), 478 (s), 487 (m), 506 (m), 531 (m), 564 (m), 587 (m), 623 (s), 765 (s), 772 (s), 1041 (vs), 1128 (vs), 1589 (w). $^1H$ NMR ([$^2H$]chloroform, 293 K): $\delta$ 1.72 (s, $Me_{C\wedge P}$), 1.77 (s, $Me_{3,5-dmpz}$), 2.28 (s, $Me_{3,5-dmpz}$), 2.65 (s, $Me_{C\wedge P}$), 2.69 (d, $^2J_{HH} = 17.9$ Hz, $^2J_{PtH} = 96.92$ Hz, $CH_2$), 4.01 (d, $^2J_{HH} = 17.9$ Hz, $^2J_{PtH} = 115.8$ Hz, $CH_2$), 5.82 (s, $H^4$), 6.0−7.8 (m, $C_6H_4$). MS ($FAB^+$, $CH_2Cl_2$; *m*/*z*; %): 1295, 100% ($M^+$).

**[{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-4-Mepz)}$_2$Ag]$ClO_4$ (4c).** To a solution of [{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-4-Mepz)}$_2$] (**2c**; 0.2087 g, 0.18 mmol) in $CH_2Cl_2$ (20 mL) was added $AgClO_4$ (0.045 g, 0.22 mmol) and $OEt_2$ (5 mL), and the mixture was stirred in the dark at room temperature for 2 h. Then, the mixture was filtered through Celite and the resulting solution was evaporated to dryness. The addition of diethyl ether to the residue gave **4c** as a pale yellow solid (0.195 g, 79% yield). Anal. Found: C, 44.08; H, 4.35; N. 4.00. Calcd for $AgC_{50}ClH_{50}N_4O_4P_2Pt_2$: C, 43.95; H, 3.69; N, 4.09. $\Lambda_M = 131\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($1.27 \times 10^{-4}$ M, acetone). IR ($\nu_{max}/cm^{-1}$): 463 (w), 478 (m), 529 (m), 565 (w), 588 (w), 625 (m), 766 (s), 1094 (vs), 1587 (w). $^1H$ NMR ([$^2H$]dichloromethane, 293 K): $\delta$ 1.47 (s, $Me_{C\wedge P}$), 1.95 (s, $Me_{4-Mepz}$), 2.90 (s, $Me_{C\wedge P}$), 3.21 (d, $^2J_{HH} = 20.0$ Hz, $^2J_{PtH} = 70.0$ Hz, $CH_2$), 3.98 (d, $^2J_{HH} = 17.9$ Hz, $^2J_{PtH} = 120.0$ Hz, $CH_2$), 5.82 (s, $H^4$), 6.0−7.8 (m, $C_6H_4$). MS ($FAB^+$, $CH_2Cl_2$; *m*/*z*; %): 1266, 100% ($M^+$).

**[{Pd{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-3,5-dmpz)}$_2$Ag]$ClO_4$ (5).** The synthesis and structural NMR data have already been published.[24] $\Lambda_M = 10.7\ \Omega^{-1}\ cm^2\ mol^{-1}$ ($10^{-3}$ M, 1,2-dichloroethane). IR ($\nu_{max}/cm^{-1}$): 456 (m), 471 (s), 483 (s), 504 (w), 527 (s), 560 (m), 586 (m), 622 (s), 751 (s), 762 (s, sh), 1063 (vs), 1133 (vs), 1585 (m). MS ($FAB^+$, $CH_2Cl_2$; *m*/*z*; %): 1119, 100% ($M^+$).

**Crystal Structure Analysis of [{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-4-Mepz)}$_2$Ag]$ClO_4$·$2CHCl_3$ (4c·$2CHCl_3$).** Crystal data and other details of the structure analysis are presented in Table 1. Suitable crystals of **4c** were obtained by slow diffusion of *n*-hexane into a solution of 0.025 g of [{Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-4-Mepz)}$_2$Ag]$ClO_4$ in $CH_2Cl_2$ (3 mL) and were mounted at the end of a glass fiber. Unit cell dimensions were determined from 25 centered reflections in the range $22.0 < 2\theta < 31.5°$, each centered at four different goniometer positions. An absorption correction was applied on the basis of 548 azimuthal scan data.

The structure was solved by Patterson and Fourier methods. All refinements were carried out using the program SHELXL-93.[27] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters of 1.2 times the $U_{iso}$ value of their attached carbon atoms (1.5 times for methyl hydrogen atoms). Full-matrix least-squares refinement of this model against $F^2$ converged to the final residual indices given in Table 1. Final difference electron density maps showed no features above 1 e/Å$^3$ (maximum/minimum +0.96/−1.46 e/Å$^3$).

**Table 1. Crystal Data and Structure Refinement for 4c·$2CHCl_3$**

| | |
|---|---|
| empirical formula | $C_{50}H_{50}AgClN_4O_4P_2Pt_2$·$2CHCl_3$ |
| unit cell dimensions | |
| *a* (Å) | 14.2550(16) |
| *b* (Å) | 14.5969(16) |
| *c* (Å) | 26.869(4) |
| *β* (deg) | 97.305(17) |
| *V* (Å$^3$), *Z* | 5545.6(11), 4 |
| wavelength (Å) | 0.710 73 |
| temp (K) | 150(1) |
| radiation | graphite-monochromated Mo Kα |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| cryst dimens (mm) | 0.38 × 0.32 × 0.27 |
| abs coeff ($mm^{-1}$) | 5.826 |
| transmissn factors | 0.929, 0.645 |
| abs cor | *ψ* scans |
| diffractometer | Enraf-Nonius CAD4 |
| 2*θ* range for data collection (deg) | 4.0−50.0 (+*h*, +*k*, ±*l*) |
| no. of rflns collected | 10 171 |
| no. of indep rflns | 9751 (*R*(int) = 0.0376) |
| refinement method | full-matrix least squares on $F^2$ |
| goodness of fit on $F^2$ | 1.031 |
| final *R* indices ($I > 2\sigma(I)$)[a] | R1 = 0.0375<br>wR2 = 0.0848 |
| *R* indices (all data) | R1 = 0.0597<br>wR2 = 0.0928 |

[a] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

## Results and Discussion

**Synthesis and Characterization of the Complexes [{M{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-Rpz)}$_2$] (M = Pt, Rpz = pz (2a), 3,5-dmpz (2b), 4-Mepz (2c); M = Pd, Rpz = pz (3a), 3,5-dmpz (3b), 4-Mepz (3c)).** Complexes **2a**−**c** and **3a**−**c** have been prepared in good yield by reaction of the corresponding dinuclear acetate bridging derivatives, [{M{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-$O_2CCH_3$)}$_2$] (M = Pt (**1a**), Pd (**1b**)) with an excess of pyrazole (Hpz), 3,5-dimethylpyrazole (H3,5-dmpz), or 4-methylpyrazole (H4-Mepz) in refluxing methanol and in the presence of triethylamine (Scheme 1). Elemental analyses and IR and NMR data are given in the Experimental Section. The mass spectra ($FAB^+$) of these complexes are those expected for the dinuclear formulation. According to this formulation such compounds could exist as two different isomers: cis and trans. The $^{31}P\{^1H\}$ NMR spectra of these compounds at room temperature (20 °C) in $CDCl_3$ display in all cases only one singlet, which for **2a**−**c** is flanked by the corresponding platinum satellites ($J_{Pt-P}$ = ca. 4000 Hz) (Table 2). The $^1H$ NMR spectra (similar experimental conditions) also confirm the equivalence of the halves of the molecules (see Experimental Section). In addition, the presence of only one singlet due to $H^4$ (or to 4-Me) of both pyrazolate rings indicates that these complexes have a trans configuration. If these complexes were the cis isomers, their $^1H$ NMR spectra should show two signals, as the two rings would be magnetically nonequivalent. The assignments of the $CH_3$ signals of the respective molecules were made through NOESY experiments.

The $^{31}P$ and $^1H$ NMR spectra of [{M{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*κC,P*}(*μ*-3,5-dmpz)}$_2$] (M = Pt (**2b**), Pd, (**3b**)) in

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[27] Sheldrick, G. M. SHELXL 93; University of Göttingen, Göttingen, Germany.

**Scheme 1**

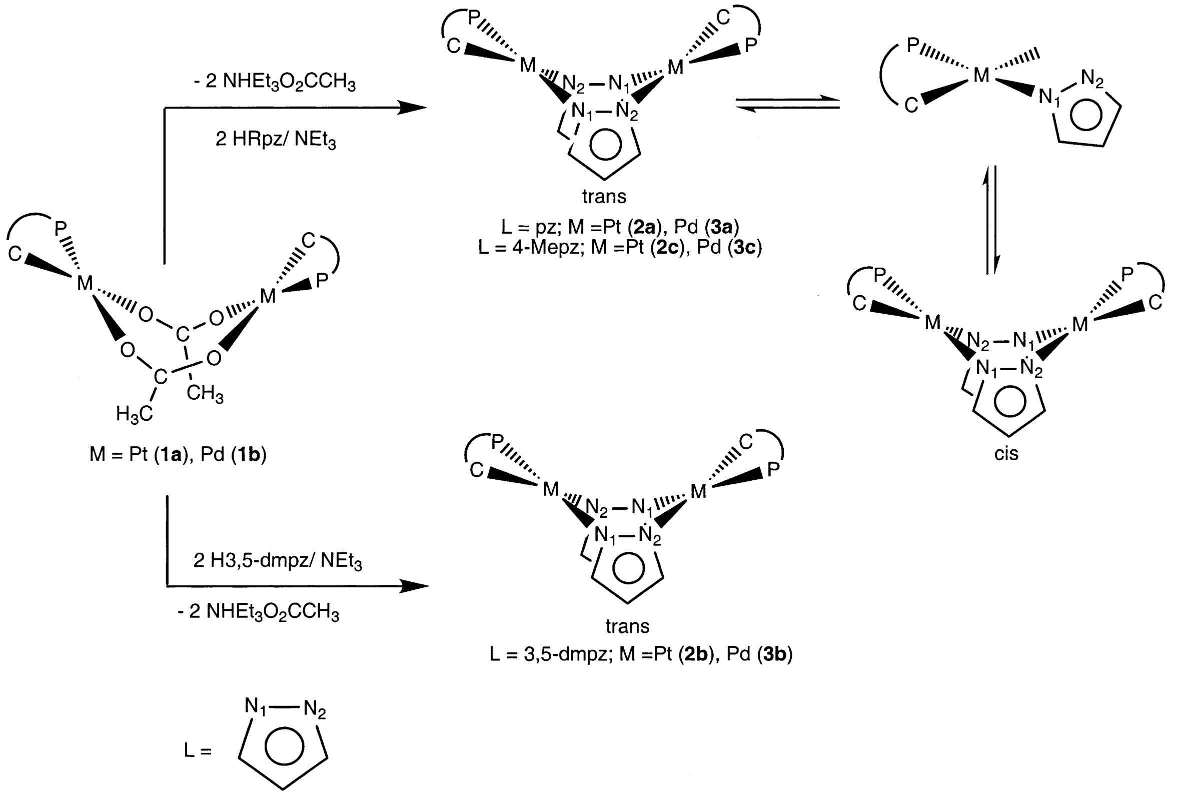


**Table 2. $^{31}P\{^1H\}$ NMR Data**

| complex | $\delta$(P) (ppm) | $\Delta(\delta(P))$ (ppm) | $^1J_{Pt-P}$ (Hz) | $\Delta(^1J_{Pt-P})$ (Hz) |
|---|---|---|---|---|
| $[\{Pt(C\wedge P)(\mu\text{-}O_2CCH_3)\}_2]$ (**1a**)[a,b] | 8.42 (s) | | 5311.0 | |
| $[\{Pt(C\wedge P)(\mu\text{-pz})\}_2]$ (**2a**)[c] | 19.39 (s) | | 3957.4 | |
| $[\{Pt(C\wedge P)(\mu\text{-}3,5\text{-dmpz})\}_2]$ (**2b**)[c] | 18.72 (s) | | 4026.9 | |
| $[\{Pt(C\wedge P)(\mu\text{-}4\text{-Mepz})\}_2]$ (**2c**)[c] | 19.47 (s) | | 3951.0 | |
| $[\{Pd(C\wedge P)(\mu\text{-pz})\}_2]$ (**3a**)[c] | 36.60 (s) | | | |
| $[\{Pd(C\wedge P)(\mu\text{-}3,5\text{-dmpz})\}_2]$ (**3b**)[c] | 35.61 (s) | | | |
| $[\{Pd(C\wedge P)(\mu\text{-}4\text{-Mepz})\}_2]$ (**3c**)[d] | 36.48 (s) | | | |
| $[\{Pt_2(C\wedge P)_2(\mu\text{-pz})_2Ag]\ ClO_4$ (**4a**)[c] | 14.10 (s) | −5.29 | 3383.9 | −573.5 |
| $[\{Pt_2(C\wedge P)_2(\mu\text{-}3,5\text{-dmpz})_2Ag]\ ClO_4$ (**4b**)[c] | 9.39 (s) | −9.33 | 3294.9 | −732.0 |
| $[\{Pt_2(C\wedge P)_2(\mu\text{-}4\text{-Mepz})_2Ag]\ ClO_4$ (**4c**)[d] | 11.91 (s) | −7.56 | 3342.3 | −608.7 |
| $[\{Pd_2(C\wedge P)_2(\mu\text{-}3,5\text{-dmpz})_2Ag(ClO_4)\}_2]$ (**5**)[c] | 39.13 (s) | 2.53 | | |

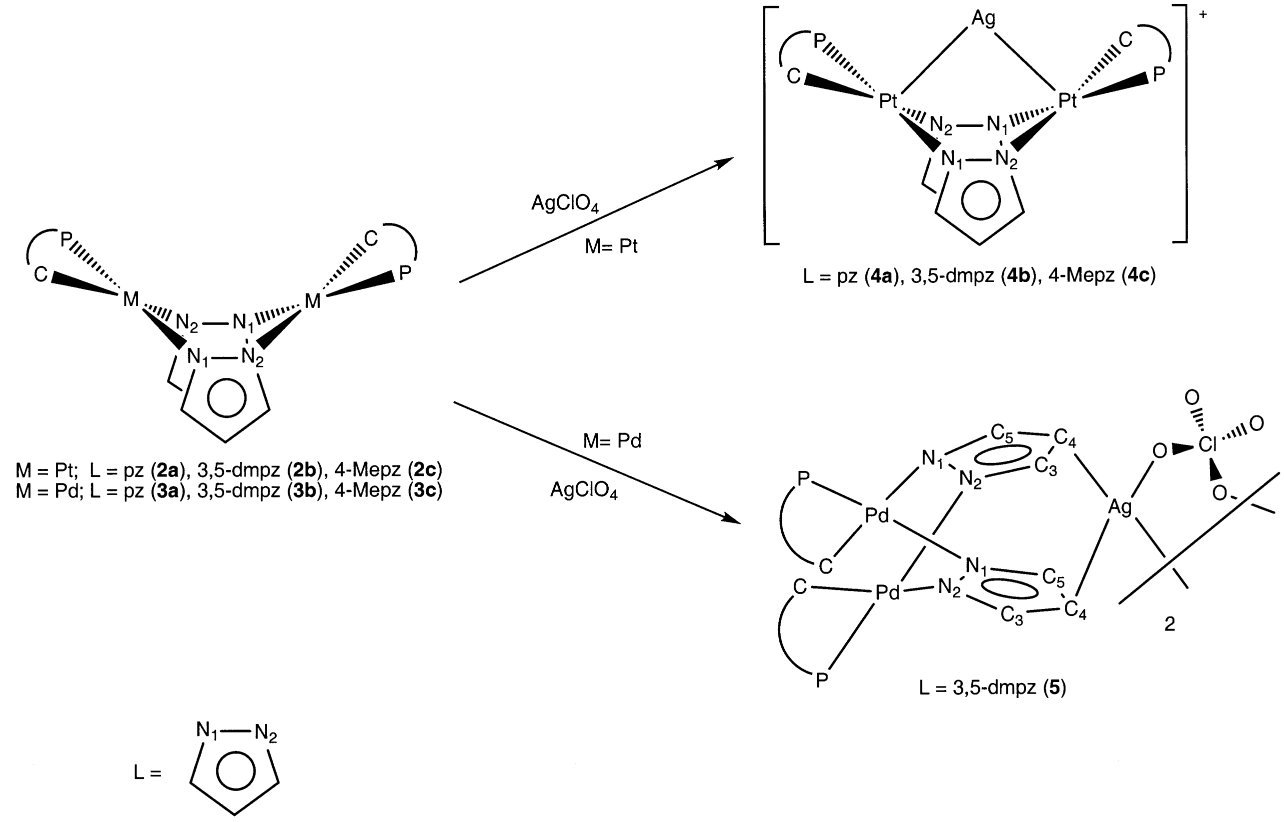
[a] $C\wedge P = CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P$. [b] Conditions: $CDCl_3$, 218 K. [c] Conditions: $CDCl_3$, 293 K. [d] Conditions: $CD_2Cl_2$, 293 K.

$CDCl_3$ are temperature-independent (range −60 to 20 °C), indicating that throughout this range only the trans isomer is present in solution. However, the $^{31}P$ NMR spectra of $[\{M\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}(\mu\text{-Rpz})\}_2]$ (M = Pt, Rpz = pz (**2a**), 4-Mepz (**2c**); M = Pd, Rpz = pz (**3a**), 4-Mepz (**3c**)) at −50 °C show three singlets, two of them (**2a**, 17.53 (s), 28.93 (s) ppm; **2c**, 17.25 (s), 29.00 (s) ppm; **3a**, 34.91 (s), 48.88 (s) ppm; **3c**, 34.52 (s), 48.82 (s) ppm) due to the cis isomer, in which the halves of the molecules are inequivalent, probably due to the hindered rotation of the *o*-tolyl groups about the P−C bonds. The other signal (**2a**, 17.74 (s) ppm; **2c**, 19.00 (s) ppm; **3a**, 35.88 (s) ppm; **3c**, 35.59 (s) ppm) corresponds to the trans isomer, in which the P−C bond rotation is not prevented. As the temperature increases, the intensity of the singlets due to the cis isomer decreases identically, while the singlet due to the trans isomer grows, remaining as the only signal observed at room temperature. This fact indicates (a) that complexes **2a, 3a** (Rpz = pz) and **2c**, **3c** (Rpz = 4-Mepz) are present in solution as a mixture of two isomers (cis and trans), which interconvert with each other very quickly, probably through mononuclear species (Scheme 1), and (b) that the trans isomer is the only species detected at 20 °C. The $^1H$ NMR spectra of **2a**,**c** and **3a**,**c** at low temperatures are also fully compatible with this behavior.

A crystallographic analysis of **2a** at 5 °C reveals a cis structure for this complex in the solid state. Because of poor data quality, the results are not suitable for publication, but the connectivity and the characteristic boatlike conformation of the six-membered "$Pt_2N_4$" metallacycle can be unambiguously established.

**Reactivity of the Platinum Derivatives $[\{Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}(\mu\text{-Rpz})\}_2]$ (Rpz = pz (2a), 3,5-dmpz (2b), 4-Mepz (2c)) toward Ag(I) Species.** $[\{Pt(C\wedge P)\ (\mu\text{-Rpz})\}_2]$ (Rpz = pz (**2a**), 3,5-dmpz (**2b**), 4-Mepz (**2c**)) react with equimolar amounts of $AgClO_4$ in $CH_2Cl_2/OEt_2$ to afford the complexes $[\{Pt(C\wedge P)(\mu\text{-Rpz})\}_2Ag]ClO_4$ (Rpz = pz (**4a**), 3,5-dmpz (**4b**), 4-Mepz (**4c**)) in high yield, as indicated in Scheme 2. The

**Scheme 2**



reactions of complexes **2a**−**c** with greater quantities of $AgClO_4$ (molar ratio 1:3) also yield the same compounds, **4a**−**c**, which indicates that complexes **2a**−**c** incorporate only one silver atom each. Additionally, complexes **2a**−**c** react with $[Ag(OClO_3)(PPh_3)]$ in a 1:2 molar ratio to give, again, compounds **4a**−**c**, with $[Ag(PPh_3)_2]ClO_4$ as a byproduct. These compounds (**4a**−**c**) are pale yellow air- and moisture-stable crystalline solids and have been characterized by analytical and spectroscopic methods and also by a single-crystal X-ray diffraction study on compound **4c**.

Mass spectra of compounds **4a**−**c** show a high peak ($I = 100\%$) corresponding to the cationic species $[\{Pt(C{\wedge}P)\ (\mu\text{-}Rpz)\}_2Ag]^+$ ($m/z$ 1239 (**4a**), 1295 (**4b**), 1266 (**4c**)). The molar conductivities of the three compounds are appropriate for 1:1 electrolytes.

The structure of the cation of **4c** is shown in Figure 1, together with the atom-labeling scheme and bond distances and angles. The trinuclear platinum−silver $[Pt_2Ag]$ cation is comprised of the dinuclear platinum starting material "$[Pt_2\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}_2(\mu\text{-4-Mepz})_2]$" and a silver cation bonded to both platinum centers and to two *o*-tolyl rings through their $\pi$ electron density, in such a way that the Ag atom can be considered to be trapped in the $[Pt_2]$ unit.

The platinum fragment is comprised of two "$Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P\}$" metallacycles bridged by two 4-Mepz ligands. The Pt···Pt separation (3.402(1) Å) precludes any intermetallic interaction. The six-membered ring $Pt_2N_4$ has, as expected, a boat conformation, the angle between the two Pt−N−N−Pt fragments being 75.7°.[28] This conformation creates an "open book" disposition for the square-planar environments of the two platinum atoms (as in the starting material). The dihedral angle between the best least-squares planes of the platinum environments is 97.2°. This disposition creates an appropriate site for the silver atom to be located, two Pt−Ag donor−acceptor bonds being established. The Pt−Ag bond distances are 2.783(1) Å (Pt(1)−Ag) and 2.788(1) Å (Pt(2)−Ag), within the range found for this kind of donor−acceptor bond.[6,8,11,29] The Pt−Ag vectors are roughly perpendicular to the coordination planes of their respective Pt atoms; the angle between the Pt−Ag bond and the perpendicular to the Pt coordination plane has, in both cases, a value of 11.5°.[28] This structural parameter is also indicative of a good orbital overlap to form the Pt−Ag bond.[30]

The Pt(1)−Ag−Pt(2) angle is 75.28(2)°, similar to those found in other complexes in which a dinuclear Pt complex acts as a chelating ligand toward silver, for instance in $[Pt_2Ag(\mu\text{-}Cl)_2(C_6F_5)_4(OEt_2)]^-$ (Pt(1)−Ag−Pt(2) = 72.15°)[6] and $[(C_6F_5)_2Pt(\mu\text{-}OH)(\mu\text{-dppm})\{Ag(PPh_3)\}Pt(C_6F_5)_2]^-$ (Pt(1)−Ag−Pt(2) = 76.4°).[31]

The silver atom completes its coordination sphere with additional interactions to the $\pi$ electron density of two *o*-tolyl groups, one from each C∧P group. Two short Ag−C distances to each *o*-tolyl group are observed: 2.498(7) Å (C(37)) and 2.609(7) Å (C(42)) for one *o*-tolyl group and 2.528(7) Å (C(16)) and 2.748(1) Å (C(17)) for the other. The remaining silver−carbon separations are greater than 3.00 Å, well beyond the limits from 2.42

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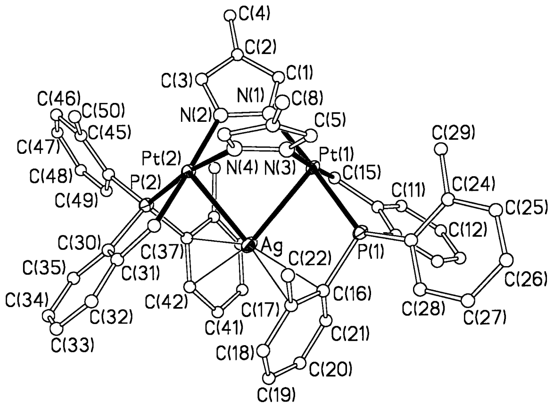

**Figure 1.** Molecular structure and numbering scheme for **4c.** Selected bond lengths (Å) and angles (deg) for **4c**·2$CHCl_3$: Pt(1)−Ag = 2.783(1), Pt(2)−Ag = 2.788(1), Pt(1)−P(1) = 2.229(2), Pt(1)−C(15) = 2.055(7) Pt(1)−N(1) = 2.070(6), Pt(1)−N(3) = 2.093(6), Pt(2)−P(2) = 2.227(2), Pt(2)−C(36) = 2.068(7), Pt(2)−N(2) = 2.085(5), Pt(2)−N(4) = 2.068(5), Ag−C(16) = 2.528(7), Ag−C(17) = 2.748(1), Ag−C(37) = 2.498(7), Ag−C(42) = 2.609(7); C(15)−Pt(1)−N(1) = 88.0(3), N(1)−Pt(1)−N(3) = 87.4(2), C(15)−Pt(1)−P(1) = 84.3(2), N(3)−Pt(1)−P(1) = 100.43(16), C(15)−Pt(1)−Ag = 87.7(2), N(1)−Pt(1)−Ag = 99.07(16), N(3)−Pt(1)−Ag = 94.91(15), P(1)−Pt(1)−Ag = 77.21(5), C(36)−Pt(2)−N(4) = 89.3(3), N(4)−Pt(2)−N(2) = 86.6(2), C(36)−Pt(2)−P(2) = 84.8(2), N(2)−Pt(2)−P(2) = 99.75(15), C(36)−Pt(2)−Ag = 86.6(2), N(4)−Pt(2)−Ag = 96.62(16), N(2)−Pt(2)−Ag = 97.74(16), P(2)−Pt(2)−Ag = 76.55(5), Pt(1)−Ag−Pt(2) = 75.28(2), Pt(1)−Ag−C(16) = 79.05(16), Pt(2)−Ag−C(37) = 77.86(16), C(37)−Ag−C(42) = 31.9(2), C(16)−Ag−C(42) = 120.8(2), C(16)−Ag−C(37) = 149.5(2), Pt(2)−Ag−C(42) = 100.43(17).

to 2.76 Å observed in previously reported $Ag^I-\eta$-aryl complexes.[32−40] Thus, from the shortest Ag−C distances, it can be construed than the two *o*-tolyl groups are $\eta^2$-bonded to the silver center. In accord with a common feature found in complexes with this kind of aryl−metal interaction[36−40] the two *o*-tolyl rings show asymmetrical $\eta^2$-aryl−silver bonds; the corresponding Ag−C lines form angles with the perpendicular to the aryl ring, of 6.8 and 24.3° for C(16) and C(17) and of 12.1 and 21.3° for C(37) and C(42), respectively. Longer Ag−C distances correspond to larger deviations of the Ag atom from the line perpendicular to the aryl ring, drawn through the corresponding C atom. The coordinated phenyl groups maintain their planarity, and the C−C distances in the rings are equal within experimental error.[28] This indicates that, despite the $\eta^2$-arene−Ag coordination, the aromaticity of the coordinated aryl ring is maintained, and further suggests a weak Ag−arene interaction.

The $^{31}P\{^1H\}$ NMR spectra of complexes **4a**−**c** (see Table 2) show only one singlet between 9 and 15 ppm flanked by the corresponding $^{195}Pt$ satellites, indicating that the halves of the molecule are equivalent in solution. These signals appear at lower frequencies, and the $^{195}Pt-P$ coupling constants are smaller, than those observed in the respective starting materials ($\Delta J_{Pt-P}$ range 570−735 Hz). As was the case in the complexes [Pt(C∧P)($S_2CZ$)HgX(μ-X)$]_2$ (Z = $NMe_2$, OEt; X = Br, I),[21] [Pt(C∧P)(acac-*O*,*O*′)HgI(μ-I)$]_2$, and [{Pt(C∧P)(acac-*O*,*O*′)-HgBr(μ-Br)$\}_2$(μ-$HgBr_2$)],[22] the decrease observed in the $^{195}Pt-P$ coupling constant occurs when the Pt atoms are involved in a Pt to M (M = Hg, Ag) donor−acceptor bond.

Keeping in mind that the compounds [{Pt(C∧P)(μ-Rpz)$\}_2$] (Rpz = pz (**2a**), 3,5-dmpz (**2b**), 4-Mepz (**2c**)) react with [Ag($OClO_3$)($PPh_3$)] in a 1:2 molar ratio to afford the complexes [{Pt(C∧P)(μ-Rpz)$\}_2$Ag]$ClO_4$ (Rpz = pz (**4a**), 3,5-dmpz (**4b**), 4-Mepz (**4c**)), with [Ag($PPh_3$$)_2$]$ClO_4$ as a byproduct, it is worth emphasizing the following. The strength of $\eta^1$-arene− or $\eta^2$-arene−metal interactions depends on the nature of both the arene and the complex fragment, but they are normally weak in nature,[41] since this kind of interaction can be broken easily by weak donor ligands.[42−45] Surprisingly, in our case, the opposite holds, since the $PPh_3$ ligand is replaced from the coordination sphere of the Ag atom by the π electron density of two aromatic rings. As a result, this $PPh_3$ ligand bonds to another Ag atom to form [Ag($PPh_3$$)_2$]$ClO_4$ as a byproduct.

**Reactivity of the Palladium Derivatives [{Pd{$CH_2C_6H_4P$(*o*-tolyl)$_2$-κ*C*,*P*}(μ-Rpz)$\}_2$] (Rpz = pz (3a), 3,5-dmpz (3b), 4-Mepz (3c)) toward $AgClO_4$.** Complexes **3a**,**c** do not react with $AgClO_4$ in any molar ratio, while the reaction of [$Pd_2$(C∧P$)_2$(μ-3,5-dmpz$)_2$] (**3b**) with $AgClO_4$ gives [{$Pd_2$(C∧P$)_2$($\mu^3$-3,5-dmpz-*N*,*N*′,$C^4$$)_2$Ag-($\mu^2$-$\eta^2$-$ClO_4$)$\}_2$] (**5**), as is indicated in Scheme 2.

The molecular structure of **5**, determined by X-ray diffraction, has been communicated.[24] The molecule is represented in Scheme 2. The structure of complex **5** is completely different from that of the Pt complexes, since neither Pd−Ag nor *o*-tolyl arene−Ag interactions are present.

The extraordinary structural feature of this compound is the unprecedented coordination mode of the 3,5-dmpz groups to $Ag^+$. The silver cation is located in the cleft between, and approximately equidistant from, the two 3,5-dmpz rings at distances of 2.410(5) and 2.420(5) Å from the respective $C^4$ atoms (Scheme 2). Thus, both 3,5-dmpz rings are $\eta^1$-coordinated ($C^4$ ) to the silver atom. Despite the $\eta^1$ interaction to the silver center, the pyrazolato rings maintain their aromaticity, as the bond distances and angles in the dmpz groups in **5** are very similar to those observed in uncomplexed "$M_2L_2$(μ-pz$)_2$"

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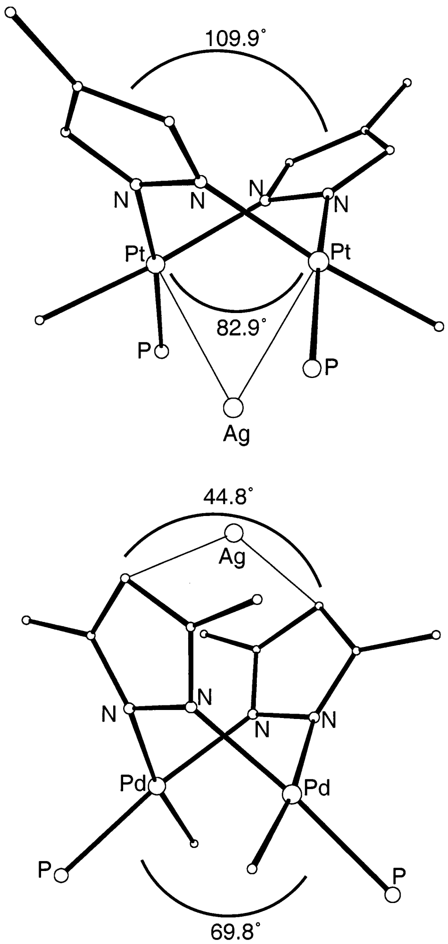

**Figure 2.**

compounds. The mass spectrum (FAB$^+$) of **5** shows the molecular peak for the cation [$Pd_2(C{\wedge}P)_2(\mu^3$-3,5-dmpz-$N,N'C^4)_2Ag]^+$ (*m*/*z* 1119). The sharp $^{31}P$, $^1H$, and $^{13}C$ NMR signals of **5** at room temperature and their observed shifts with respect to those in the starting material, **3b**, indicate that the silver–$\eta^1$-dmpz bonds are present in solution.

## Concluding Remarks

The ability of the neutral dinuclear platinum azolato complexes **2a**–**c** to participate in the formation of Pt→Ag bonds is obvious.

The reactivity of the analogous palladium derivatives toward $AgClO_4$ is much reduced, since two of them do not allow isolation of any silver adduct and [$Pd_2(C{\wedge}P)_2(\mu$-3,5-dmpz$)_2$] (**3b**) forms a very unusual Pd/Ag adduct with the silver cation locked into the cleft between the two dmpz groups through two $\eta^1$-$C^4$–Ag bonds.

The Pt- and Pd-containing starting materials display remarkable flexibility in adapting to the coordination of $Ag^+$. The platinum complexes form two Pt→Ag donor–acceptor bonds using the $d_{z^2}$ electron density on Pt, an interaction that is optimized when Ag lies on the line perpendicular to the platinum coordination plane. Together with the constraints imposed by the bridging pyrazolyl ligands, this leads to a dihedral angle of 82.9° between the two platinum coordination planes for **4c**, as compared to the value of 69.8° found for the palladium complex **5**, which lacks Pd–Ag bonds. For the Pd-containing product, the two $\eta^1$-C–Ag bonds lead to a dihedral angle of 44.8° between the dmpz rings. This can be compared to the value of 109.9° for the platinum complex, in which the dmpz groups do not accommodate the silver atom (Figure 2).

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**Supporting Information Available:** Tables of atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, all bond distances and bond angles, and hydrogen coordinates and isotropic displacement parameters for the crystal structure of complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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