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Reactions of di- and tri-nuclear palladium and platinum isocyanide complexes with highly basic and bulky aromatic phosphines containing methoxy groups at the 2 and 6 positions

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Reactions of $[M_2(RNC)_6]^{2+}$ (M = Pd **1** or Pt **3**) (R = 2,6-$Me_2C_6H_3$) with L = tris(2,6-dimethoxyphenyl)phosphine, bis(2,6-dimethoxyphenyl)phenylphosphine or (2,6-dimethoxyphenyl)diphenylphosphine gave $[M_2(RNC)_4L_2]^{2+}$ (M = Pd **2** or Pt **4**). Reaction of the neutral complex $[Pd_2Cl_2(RNC)_4]$ **5** with $P[C_6H_3(OMe)_2]_3$ gave $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2]Cl_2$ **6c**. A similar reaction in the presence of NH_4PF_6 gave **2c** {L = $P[C_6H_3(OMe)_2]_3$} and *trans*-$[PdCl(RNC)_2\{P[C_6H_3(OMe)_2]_3\}]^+$ **7c**. Compound **7c** was obtained from the secondary reaction of **2c** with NH_4Cl formed initially. The structure was confirmed by an X-ray analysis. The trinuclear complex $[Pt_3(RNC)_8]^{2+}$ reacted with the phosphines to give corresponding $[Pt_3(RNC)_6L_2]^{2+}$. A similar reaction of $[Pd_3(RNC)_8]^{2+}$ with $PPh_2[C_6H_3(OMe)_2]$ or $PPh[C_6H_3(OMe)_2]_2$ produced the corresponding $[Pd_3(RNC)_6L_2]^{2+}$, whereas with $P[C_6H_3(OMe)_2]_3$ cleavage of metal–metal bonds occurred to give only **2c**.

The compound tris(2,4,6-trimethoxyphenyl)phosphine has extreme nucleophilicity and large cone angle because of the two methoxy groups at the *ortho* positions, and showed unusual reactivity towards metals.[1] Additional binding sites (oxygen co-ordination) at the phosphorus site for a metal enhance the stability of the products whereas the large cone angle and weak metal–ether O interactions increase reactivity at the metal centre. When co-ordinated to Groups 6 and 8–12 metals, $P[C_6H_2(OMe)_3\text{-}2,4,6]_3$ produces a variety of neutral complexes with (P), (P,OMe) and (P,OMe,OMe) co-ordinations.[2] Some complexes also contain metal–phenoxide bonds derived by elimination of one methyl residue from a methoxy group.[2e,3] Dunbar and Sun[4] reported that the complex $[Pd\{P[C_6H_2(OMe)_3]_3\}_2][BF_4]_2$, obtained from $[Pd(MeCN)_4][BF_4]_2$ and the phosphine has a distorted-octahedral geometry containing four ether-O interactions, whereas the reaction with $[Ni(MeCN)_6][PF_6]_2$ resulted in elimination of methyl moieties to give a four-co-ordinated complex $[Ni\{P[2\text{-}OC_6H_2(OMe)_2\text{-}4,6][C_6H_2(OMe)_3\text{-}2,4,6]_2\}_2]$.[5] Upon oxidation to the corresponding monocation the co-ordination number increases to six, with two additional ether-O interactions in axial positions.[5] Studies on $P[C_6H_2(OMe)_3]_3$ have been widespread, whereas the chemistry of the related tris(2,6-dimethoxyphenyl)phosphine is less well known. Its reactions with η^3-allyl-palladium and -platinum complexes gave (P), (P,ether-O) and (P,O) complexes, depending on the reaction conditions and metal.[6]

Recently we reported that $[\{RuCl_2(\eta^6\text{-arene})\}_2]$ reacted with highly basic and bulky phosphines such as $P[C_6H_3(OMe)_2]_3$, bis(2,6-dimethoxyphenyl)phenylphosphine, and (2,6-dimethoxyphenyl)diphenylphosphine to produce complexes with the neutral (P) and (P,OMe) and anionic (P,O) and (P,O,O) co-ordination accompanied by cleavage of chloride bridges and elimination of methyl chloride, depending on the phosphine, arene and reaction conditions.[7] The co-ordination mode (P,O,O) was the first example to be found for bulky phosphines having methoxy groups at the 2 and 6 positions. In an attempt to investigate the reactivity of aromatic phosphines having methoxy groups at these positions, the reactions of mono-, di- and tri-nuclear palladium and platinum isocyanide complexes with these three phosphines were carried out, and in this paper we report the preparation of palladium and platinium complexes with mixed isocyanide and bulky phosphine ligands.

Experimental

All solvents were distilled over calcium hydride. Isocyanide $CNC_6H_3Me_2\text{-}2,6$[8] and the three phosphines[9] were prepared according to the literature. Palladium and platinum complexes, $[Pd_2Cl_2(RNC)_4]$, $[M_2(RNC)_6][PF_6]_2$, $[Pd_2(RNC)_4(PPh_3)_2][PF_6]_2$ and $[M_3(RNC)_8][PF_6]_2$ (M = Pd or Pt, R = 2,6-$Me_2C_6H_3$) were prepared as described in the literature.[10,11] Infrared and electronic absorption spectra were recorded on FT/IR-5300 and U-best 30 spectrometers, respectively, NMR spectra on a Bruker AC250. Proton chemical shifts were measured relative to $SiMe_4$ using solvent resonances as standard locks, $^{31}P\text{-}\{^1H\}$ spectra using 85% H_3PO_4 as an external reference.

Reactions

$[Pd_2(RNC)_6][PF_6]_2$ with $PPh[C_6H_3(OMe)_2\text{-}2,6]_2$. A solution of the phosphine (38 mg, 0.099 mmol) in acetone (5 cm^3) was added to a solution of $[Pd_2(RNC)_6][PF_6]_2$ (60 mg, 0.047 mmol) in acetone (10 cm^3) at room temperature. After the mixture was stirred for 2 h the solvent was removed under reduced pressure and the residue crystallized from CH_2Cl_2 and Et_2O to give yellow crystals (67 mg, 80%) of $[Pd_2(RNC)_4\{PPh[C_6H_3(OMe)_2\}_2][PF_6]_2\cdot CH_2Cl_2$ **2b**. IR(Nujol): 2160 (N≡C) and 842 cm^{-1} (PF_6). UV/VIS (CH_2Cl_2): λ_{max} 427 (log ε 4.42), 354 (sh), 285 (4.38) and 243 nm (4.68). NMR(CD_3COCD_3): ^1H, δ 2.12 (s, 24 H, Me), 3.28 (s, 24 H, OMe), 5.61 (s, 2 H, CH_2Cl_2) and 6.53–7.50 (m, 34 H, Ph); $^{31}P\text{-}\{^1H\}$, δ −20.6 (s) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 51.85; H, 4.50; N, 3.15. Calc. for $C_{81}H_{84}Cl_2F_{12}N_4O_8P_4Pd_2$: C, 51.85; H, 4.50; N, 3.00%).

Similar reactions gave $[Pd_2(RNC)_4\{PPh_2[C_6H_3(OMe)_2]\}_2][PF_6]_2$ **2a** (yellow, 84%) and $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2][PF_6]_2$ **2c** (yellow, 93%).

Complex **2a**: IR(Nujol) 2160 (N≡C) and 839 (PF_6) cm^{-1}; UV/VIS (CH_2Cl_2) λ_{max} 420 (log ε 4.32), 353 (3.76), 270 (sh) and 250 (4.53) nm; ^1H NMR(CD_3COCD_3), δ 1.96 (s, 24 H, Me), 3.24 (s, 12 H, OMe) and 6.45–7.50 (m, 38 H, Ph); $^{31}P\text{-}\{^1H\}$

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NMR(CD_3COCD_3), δ −2.71 (s) and −144.6 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 54.35; H, 4.40; N, 3.30. Calc. for $C_{76}H_{74}F_{12}N_4O_4P_4Pd_2$: C, 54.60; H, 4.45, N, 3.35%).

Complex **2c**: IR(Nujol) 2153 (N≡C) and 842 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} 432 (4.27), 289 (4.27) and 236 nm (log ε 4.66); ^1H NMR($CDCl_3$), δ 1.98 (s, 24 H, Me), 3.15 (s, 36 H, OMe) and 6.15–7.30 (m, 30 H, Ph); $^{31}P-\{^1H\}$ NMR($CDCl_3$), δ −40.1 (s) and −144.6 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 52.70; H, 4.85; N, 3.00. Calc. for $C_{84}H_{90}F_{12}N_4O_{12}P_4Pd_2$: C, 52.75; H, 4.75; N, 2.95%).

$[Pd_2Cl_2(RNC)_4]$ with $P[C_6H_3(OMe)_2\text{-}2,6]_3$. A solution of the phosphine (119 mg, 0.27 mmol) in acetone (5 cm^3) was added to a solution of $[Pd_2Cl_2(RNC)_4]$ (103 mg, 0.13 mmol) in acetone (10 cm^3) at room temperature. After the mixture was stirred for 2 h, the solvent was reduced to *ca.* 5 cm^3 under reduced pressure and Et_2O was added to give orange crystals (170 mg, 79%) of $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2\text{-}2,6]_3\}_2]Cl_2$ **6c**. IR(Nujol): 2184 cm^{-1} (N≡C). UV/VIS (CH_2Cl_2): λ_{max} 432, 354 (sh), 284 and 241 nm. NMR($CDCl_3$): ^1H, δ 1.92 (s, 24 H, Me), 2.21 (s, 5 H_2O), 3.10 (s, 36 H, OMe) and 6.10–7.30 (m, 36 H, Ph); $^{31}P-\{^1H\}$, δ −40.2 (s) (Found: C, 56.30; H, 5.50; N, 3.10. Calc. for $C_{84}H_{100}Cl_2N_4O_{17}P_2Pd_2$: C, 56.55; H, 5.65; N, 3.15%).

When $[Pd_2Cl_2(RNC)_4]$ was treated with the other phosphines the formation of corresponding orange complexes $[Pd_2(RNC)_4\{PPh[C_6H_3(OMe)_2]\}_2]Cl_2$ and $[Pd_2(RNC)_4\{PPh_2[C_6H_3(OMe)_2]\}_2]Cl_2$ was observed spectroscopically, but they could not be isolated pure.

$[Pd_2Cl_2(RNC)_4]$ with $PPh[C_6H_3(OMe)_2]_2$ in the presence of NH_4PF_6. A solution of the phosphine (53 mg, 0.14 mmol) and NH_4PF_6 (53 mg, 0.33 mmol) in acetone (5 cm^3) was added to a solution of $[Pd_2Cl_2(RNC)_4]$ (60 mg, 0.047 mmol) in acetone (10 cm^3) at room temperature. After stirring for 2 h the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 and recrystallized from CH_2Cl_2 and Et_2O to give yellow crystals (86 mg, 71%) of complex **2b**. Analogously, the yellow compound **2a** was obtained in 87% yield.

$[Pd_2Cl_2(RNC)_4]$ with $P[C_6H_3(OMe)_2]_3$ in the presence of NH_4PF_6 or KPF_6. A solution of the phosphine (116 mg, 0.26 mmol) and NH_4PF_6 (53 mg, 0.32 mmol) in acetone (5 cm^3) was added to an acetone solution (10 cm^3) of $[Pd_2Cl_2(RNC)_4]$ (97 mg, 0.12 mmol) at room temperature. After the mixture was stirred for 2 h it was filtered to remove the precipitate. The solvent was reduced to *ca.* 3 cm^3 and Et_2O was added to give yellow crystals of complex **2c** (71 mg, 31%). Diethyl ether was added to the mother-liquor and the solution was allowed to stand in a refrigerator to yield pale yellow crystals of **7c** (34 mg, 27%): IR(Nujol) 2204 (N≡C) and 839 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} 355 (sh), 289 (sh) and 247 nm (log ε 4.66); ^1H NMR($CDCl_3$), δ 1.98 (s, 12 H, Me), 3.52 (s, 24 H, OMe) and 6.41–7.40 (m, 15 H, Ph); $^{31}P-\{^1H\}$ NMR($CDCl_3$), δ −28.3 (s), −144.6 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 50.95; H, 4.65; N, 2.80. Calc. for $C_{42}H_{45}ClF_6N_2O_6P_2Pd$: C, 50.85; H, 4.55; N, 2.80%).

When an analogous reaction was carried out using KPF_6 in place of NH_4PF_6 only compound **2c** was obtained in 62% yield.

Complex 2c with NH_4Cl in the presence of water. A mixture of $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2][PF_6]_2$ (57.3 mg, 0.0274 mmol) and NH_4Cl (17.3 mg, 0.323 mmol) in acetone (15 cm^3) and water (1 cm^3) was stirred at room temperature. After 24 h the solvent was removed to dryness and the residue extracted with CH_2Cl_2. Work-up and crystallization from CH_2Cl_2 and Et_2O gave complex **7c** (47.2 mg, 87%).

$[Pt_2(RNC)_6][PF_6]_2$ with $P[C_6H_3(OMe)_2]_3$. A solution of the phosphine (33.6 mg, 0.076 mmol) in acetone (5 cm^3) was added to a solution of $[Pt_2(RNC)_6][PF_6]_2$ (53.6 mg, 0.037 mmol) in acetone (10 cm^3) at room temperature and the mixture stirred for 2 h. The solvent was removed under reduced pressure and the residue crystallized from CH_2Cl_2 and Et_2O to give pale yellow crystals (51.3 mg, 67%) of $[Pt_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2][PF_6]_2$ **4c**. IR(Nujol): 2152 (N≡C) and 842 cm^{-1} (PF_6). UV/VIS (CH_2Cl_2): λ_{max} 382 (sh), 343, 290 and 246 nm. NMR($CDCl_3$): ^1H, δ 2.09 (s, 24 H, Me), 3.24 (s, 36 H, OMe) and 6.35–7.40 (m, Ph, 34 H); $^{31}P-\{^1H\}$, δ −17.2 ($^1J_{PtP}$ = 2287, $^2J_{PtP}$ = 471, $^3J_{PP}$ = 174) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 48.30; H, 4.40; N, 2.70. Calc. for $C_{84}H_{90}F_{12}N_4O_{12}P_4Pt_2$: C, 48.30; H, 4.35; N, 2.70%).

Analogously complexes **4a** and **4b** were obtained from the reaction of $[Pt_2(RNC)_6][PF_6]_2$ with $PPh_2[C_6H_3(OMe)_2]$ and $PPh[C_6H_3(OMe)_2]_2$.

Complex **4a** (white, 75%): IR(Nujol) 2162 (N≡C) and 841 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} 322 (4.42), 300 (4.50) and 276 nm (log ε 4.54); ^1H NMR($CDCl_3$), δ 1.94 (s, 24 H, Me), 3.18 (s, 24 H, OMe) and 6.45–7.60 (m, 34 H, Ph); $^{31}P-\{^1H\}$ NMR($CDCl_3$), δ 16.9 ($^1J_{PtP}$ = 2306, $^2J_{PtP}$ = 411, $^3J_{PP}$ = 161) and −143.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 49.15; H, 3.95; N, 3.10. Calc. for $C_{76}H_{74}F_{12}N_4O_4P_4Pt_2$: C, 49.35; H, 4.05; N, 3.05%).

Complex **4b** (yellow, 87%): IR(Nujol) 2152 (N≡C) and 841 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} *ca.* 385 (sh), 326 (4.31), 295 (sh), 280 (4.55) and 245 nm (log ε 4.61); ^1H NMR($CDCl_3$), δ 2.12 (s, 24 H, Me), 3.28 (s, 24 H, OMe) and 6.55–7.70 (m, 34 H, Ph); $^{31}P-\{^1H\}$ NMR($CDCl_3$), δ 2.29 ($^1J_{PtP}$ = 2435, $^2J_{PtP}$ = 442, $^3J_{PP}$ = 161 Hz) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 47.90; H, 4.20; N, 2.80. Calc. for $C_{80}H_{82}F_{12}N_4O_8P_4Pt_2$: C, 48.05; H, 4.15; N, 2.80%).

$[Pd_3(RNC)_8][PF_6]_2$. (*a*) *With* $P[C_6H_3(OMe)_2]_3$. A solution of the phosphine (33 mg, 0.075 mmol) in acetone (5 cm^3) was added to a solution of $[Pd_3(RNC)_8][PF_6]_2$ (62 mg, 0.037 mmol) in acetone (10 cm^3) at room temperature and the mixture stirred for 0.5 h. The solvent was removed and recrystallization of the residue from CH_2Cl_2 and Et_2O gave pale yellow crystals (31 mg, 43%) of complex **2c**.

(*b*) *With* $PPh[C_6H_3(OMe)_2]_2$ *and* $PPh_2[C_6H_3(OMe)_2]$. Analogous reaction of $[Pd_3(RNC)_8][PF_6]_2$ with the other two phosphines except the reaction time (2 h) gave yellow $[Pd_3(RNC)_6\{PPh_2[C_6H_3(OMe)_2]\}_2][PF_6]_2$ **9a** (76%) and $[Pd_3(RNC)_6\{PPh[C_6H_3(OMe)_2]_2\}_2][PF_6]_2$ **9b** (64%).

Complex **9a**: IR(Nujol) 2135 (N≡C) and 841 cm^{-1} (PF_6); UV/VIS (MeOH), λ_{max} 512 (4.08), 419 (3.95) and 249 nm (log ε 4.49); ^1H NMR(CD_3COCD_3), δ 1.94 (s, 24 H, Me), 2.56 (s, 12 H, Me), 3.31 (s, 12 H, OMe) and 6.60–7.65 (m, 44 H, Ph); $^{31}P-\{^1H\}$ NMR(CD_3COCD_3), δ 0.14 (s) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 55.05; H, 4.70; N, 4.05. Calc. for $C_{94}H_{92}F_{12}N_6O_4P_4Pd_3$: C, 55.30; H, 4.55; N, 4.10%).

Complex **9b**: IR(Nujol) 2137, 2116 (N≡C) and 841 cm^{-1} (PF_6); UV/VIS (MeOH) λ_{max} 517 (3.85), 425 (3.57) and 246 nm (log ε 4.23); ^1H NMR(CD_3COCD_3), δ 1.93 (s, 24 H, Me), 2.88 (s, 12 H, Me), 3.29 (s, 24 H, OMe) and 6.50–7.60 (m, 40 H, Ph); $^{31}P-\{^1H\}$ NMR(CD_3COCD_3), δ −16.1 (s) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 53.90; H, 4.65; N, 3.75. Calc. for $C_{98}H_{100}F_{12}N_6O_8P_4Pd_3$: C, 54.45; H, 4.65; N, 3.90%).

$[Pt_3(RNC)_6][PF_6]_2$ 10 with $P[C_6H_3(OMe)_2]_3$. To a solution of $[Pt_3(RNC)_8][PF_6]_2$ (55.6 mg, 0.037 mmol) in acetone (10 cm^3) was added the phosphine (33.6 mg, 0.76 mmol) in acetone (5 cm^3). After the mixture was stirred for 0.5 h at room temperature the solvent was reduced to *ca.* 3 cm^3 and Et_2O added to give orange crystals of complex **11c** (60.1 mg, 82%). IR(Nujol): 2133, 2108 (N≡C) and 842 cm^{-1} (PF_6). UV/VIS (CH_2Cl_2): λ_{max} 404 (3.99), 351 (4.25) and 245 nm (4.61). NMR(CD_3COCD_3): ^1H, δ 1.76 (s, 24 H, Me), 2.26 (s, 12 H, Me), 3.22 (s, 12 H, OMe) and 6.30–7.40 (m, 36 H, Ph); $^{31}P-\{^1H\}$, δ 0.26 ($^1J_{PtP}$ = 2347, $^2J_{PtP}$ = 603, $^3J_{PtP}$ = 81, $^4J_{PP}$ = 43.4) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 48.30;

H, 4.50; N, 3.25. Calc. for $C_{102}H_{108}F_{12}N_6O_{12}P_4Pt_3$: C, 48.10; H, 4.25; N, 3.30%).

Complexes **11a** (82%) and **11b** (80%) were analogously from **10** and $PPh_2[C_6H_3(OMe)_2]$ or $PPh[C_6H_3(OMe)_2]_2$.

Complex **11a**: IR(Nujol) 2133 (N≡C) and 839 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} 384 (4.18), 331 (4.22) and 281 nm (log ε 4.34); ^1H NMR(CD_3COCD_3), δ 1.94 (s, 24 H, Me), 2.55 (s, 12 H, Me), 3.25 (s, 12 H, OMe) and 6.60–7.80 (m, 44 H, Ph); $^{31}P-\{^1H\}$ NMR(CD_3COCD_3), δ 34.5 ($^1J_{PtP}$ = 2331, $^2J_{PtP}$ = 577, $^3J_{PtP}$ = 78.0, $^4J_{PP}$ = 43) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 49.25; H, 4.25; N, 3.60. Calc. for $C_{94}H_{92}F_{12}N_6O_4P_4Pt_3$: C, 48.95; H, 4.00; N, 3.65%).

Complex **11b**: IR(Nujol) 2121 (N≡C) and 839 cm^{-1} (PF_6); UV/VIS (CH_2Cl_2), λ_{max} 386, 336, 290 and 248 nm; ^1H NMR(CD_3COCD_3), δ 1.97 (s, 24 H, Me), 2.47 (s, 12 H, Me), 3.32 (s, 24 H, OMe) and 6.60–7.80 (m, 40 H, Ph); $^{31}P-\{^1H\}$ NMR(CD_3COCD_3), δ 21.7 ($^1J_{PtP}$ = 2322, $^2J_{PtP}$ = 545, $^3J_{PtP}$ = 87, $^4J_{PP}$ = 48) and −142.8 (spt, J_{PF} = 709 Hz, PF_6) (Found: C, 47.85; H, 4.10; N, 3.55%. Calc. for $C_{98}H_{100}F_{12}N_6O_8P_4Pt_3$: C, 48.50; H, 4.15; N, 3.45%).

Crystallography

Complex **7c** was recrystallized from CH_2Cl_2–Et_2O. Cell constants were determined from 25 reflections on a Rigaku four-circle AFC5S automated diffractometer. The crystal parameters along with data collection are summarized in Table 1. Intensities were measured by the 2θ–ω scan method using Mo-Kα radiation (λ = 0.710 69 Å). A scan rate of 16° min^{-1} was used. Throughout the data collection the intensities of the three standard reflections were measured every 150 as a check of the stability of the crystals, but no decay was observed. Of a total of 7959 (2θ < 50°) independent intensities measured, 6195 [$I > 3.0\sigma(I)$] reflections were used in the solution and refinement of the structure. Intensities were corrected for Lorentz-polarization effects and for absorption. A final Fourier-difference map showed no residual peaks greater than 0.72 e $Å^{-3}$ around the palladium atom. Atomic scattering factors and anomalous dispersion effects were taken from ref. 12. All calculations were performed on a Digital VAX Station 3100 M38 computer using the TEXSAN-TEXRAY program System.[13] The perspective views were drawn by the program ORTEP.[14]

The structure was solved by Patterson methods. The palladium atom was located in the initial E map, and subsequent Fourier syntheses gave the positions of the other non-hydrogen atoms. Hydrogen atoms were calculated at the ideal positions with C–H 0.95 Å, and were not refined. The positions of the non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The final refinement converged to R = 0.042 and R' = 0.052. A final Fourier-difference synthesis showed peaks at heights up to 0.72 e $Å^{-3}$. The positional parameters are given in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Dinuclear complexes

When the cationic dinuclear complex $[Pd_2(RNC)_6][PF_6]_2$ **1** (R = 2,6-$Me_2C_6H_3$) was treated with 2 equivalents of $PPh_2[C_6H_3(OMe)_2]$, $PPh[C_6H_3(OMe)_2]_2$ or $P[C_6H_3(OMe)_2]_3$ (L) at room temperature the replacement of axial isocyanide ligands readily occurred to give the corresponding yellow complexes $[Pd_2(RNC)_4L_2][PF_6]_2$ **2a**–**2c** in high yield. The infrared spectra showed a ν(N≡C) band at *ca.* 2160 cm^{-1}. The ^1H NMR spectra showed two singlets at δ *ca.* 2.00 and 3.20, due to methyl and methoxy groups, respectively and the intensity ratio between the isocyanide and phosphine ligands was 4:2. The $^{31}P-\{^1H\}$ NMR spectra showed only one singlet for the tertiary phosphine ligands at δ −2.71 (for **2a**), −20.6 (**2b**) and −40.1 (**2c**), respectively. The electronic spectra are similar to those of the parent complex **1** and the known compound $[Pd_2(RNC)_4(PPh_3)_2][PF_6]_2$ **2d**, and indicated a σ–σ* transition band near *ca.* 425 nm.

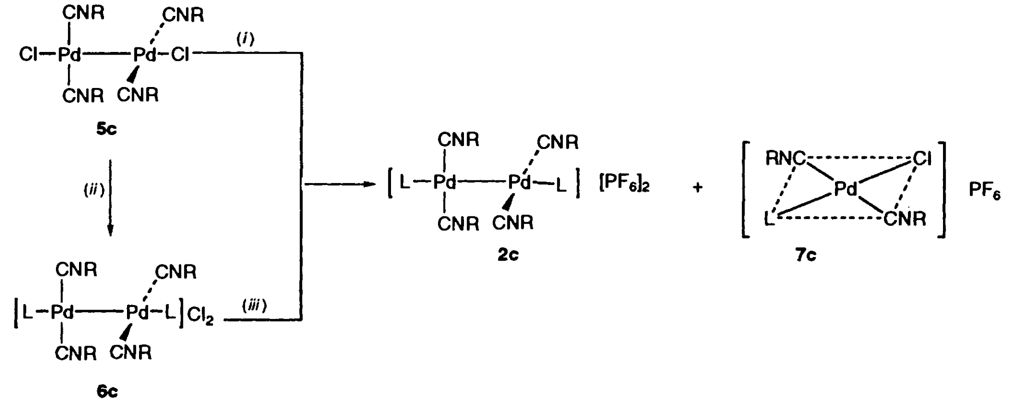
Reactions of $[Pt_2(RNC)_6][PF_6]_2$ **3** with the tertiary phosphines readily led to the replacement of axial isocyanides to form $[Pt_2(RNC)_4L_2][PF_6]_2$ **4**. In the ^1H NMR spectra two singlets for methyl and methoxy groups appeared as for the palladium analogue **2**. In the $^{31}P-\{^1H\}$ NMR spectra the patterns containing coupling with Pt atoms are in good agreement with that of the known complex $[Pt_2(RNC)_4(PPh_3)_2]^{2+}$ **4d**.[15] The electronic spectra are also similar to that of the parent complex **3**. Based on these spectroscopic studies, the dimeric complexes are assumed to have a structure in which two MPC_2 (M = Pd or Pt) planes are almost perpendicular.

Reaction of the neutral complex $[PdCl_2(RNC)_4]$ **5** with $P[C_6H_3(OMe)_2]_3$ gave an ionic complex $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2]Cl_2$ **6c** whereas in the reaction with the other two phosphines evidence for the formation of corresponding complexes **6a** and **6b** was obtained only from spectroscopic studies. A solution of compound **6a** or **6b** in acetone was treated with NH_4PF_6 to give the corresponding complex $[Pd_2(RNC)_4L_2][PF_6]_2$ **2a** or **2b** in high yields. These compounds were also obtained by direct reaction of the neutral dimeric complex **5** with the phosphine in the presence of NH_4PF_6. A similar reaction of **6c** with NH_4PF_6 gave $[PdCl(RNC)_2\{P[C_6H_3(OMe)_2]_3\}]PF_6$ **7c** (31%) in moledate yield together with **2c** (27%) (Scheme 1). The infrared spectrum of **7c** showed only one ν(N≡C) band at 2204 cm^{-1} in the region where it has often been observed for divalent palladium complexes. In the electronic spectrum the σ–σ* transition band at 432 nm for the dimeric complex **6c** disappeared and the spectral pattern corresponded to those found for divalent square-planar palladium complexes. In the ^1H NMR spectrum the methyl protons appeared at δ 1.98 as a sharp singlet, whereas the methoxy groups were observed as a broad singlet at δ 3.52, likely due to restricted rotation of the phosphine ligand. These spectral data suggested a *trans* structure. This was confirmed by an X-ray analysis (see below).

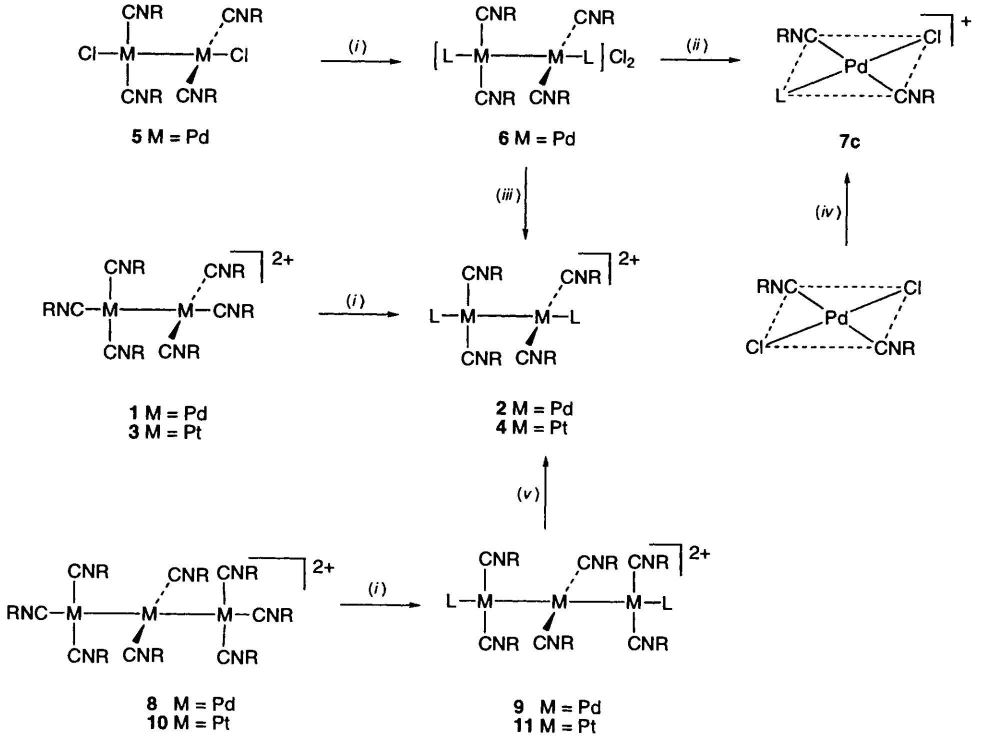
Trinuclear complexes

The treatment of the ionic trinuclear complex $[Pd_3(RNC)_8][PF_6]_2$ **8** with $PPh_2[C_6H_3(OMe)_2]$ or $PPh[C_6H_3(OMe)_2]_2$ at room temperature resulted in substitution of isocyanides at the axial positions to give reddish orange crystals formulated as $[Pd_3(RNC)_6L_2][PF_6]_2$ **9a** and **9b**. The ν(N≡C) band appeared at *ca.* 2135 cm^{-1}, *ca.* 25 cm^{-1} lower than for the dinuclear complexes. The ^1H NMR spectra showed the presence of two kinds of isocyanide ligands in a 2:1 intensity ratio. Only one singlet for phosphine ligands appeared at δ 0.14 for **9a** and δ −16.1 for **9b** in the $^{31}P-\{^1H\}$ NMR spectra. The electronic spectra are similar to that of $[Pd_3(RNC)_6(PPh_3)_2][PF_6]_2$.[10]

The reaction of complex **8** with $P[C_6H_3(OMe)_2]_3$ led to the fragmentation of the trinuclear core to give the dinuclear complex **2c**. The fate of the $Pd(RNC)_2$ fragment remains unknown at present. In an attempt to investigate this process, time-dependent electronic spectra were measured. They were reminiscent of formation of **9c** and the final spectrum was in good agreement with that of **2c**. An initial process is the substitution of axial isocyanide ligands, followed by cleavage of metal–metal bonds. Co-ordination of the $P[C_6H_3(OMe)_2]_3$ ligands weakens the metal–metal bonds because of the accumulation of electron density on them arising from the high basicity of the phosphine.



Scheme 1 Reactions of dinuclear palladium complex **5c** with $P[C_6H_3(OMe)_2\text{-}2,6]_3$ (L); R = $2,6\text{-}Me_2C_6H_3$. (*i*) L, NH_4PF_6; (*ii*) L; (*iii*) NH_4PF_6



Scheme 2 Reactions of di- and tri-nuclear complexes with tertiary phosphines (L). The anion (PF_6^-) except in **6** is omitted for clarity. R = $2,6\text{-}Me_2C_6H_3$. (*i*) L; (*ii*) PF_6^-, L = $P[C_6H_3(OMe)_2]_3$; (*iii*) PF_6^-; (*iv*) L, PF_6^-; (*v*) decomposition, M = Pd, L = $P[C_6H_3(OMe)_2]_3$

Reactions with the trinuclear platinum analogue **10** resulted in replacement of the axial isocyanides for all tertiary phosphines to give $[Pt_3(RNC)_6L_2][PF_6]_2$ **11**, owing to the stronger Pt–Pt bond. The $^{31}P\text{-}\{^1H\}$ NMR spectral patterns are comparable with that of $[Pt_3(RNC)_6(PPh_3)_2][PF_6]_2$ **11d**.[10,15] Together with the crystal structures of **11d** and $[Pd_3(MeNC)_6(PPh_3)_2][PF_6]_2$ **12**,[16] these spectral data suggested that the trinuclear compounds of palladium and platinum (**9**, **11**) have a structure in which three planes containing the Pt atoms are almost perpendicular with each other.

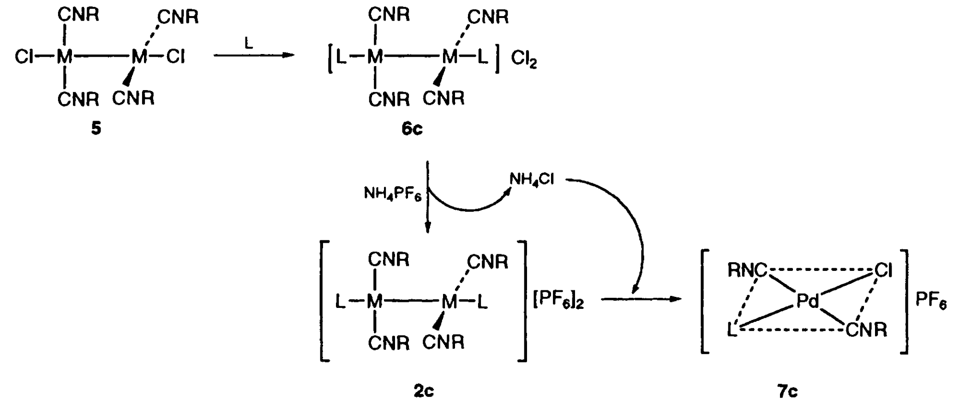
Mechanism of formation of complex 7c

The overall reactions mentioned above are summarized in Scheme 2. Some attempts to confirm a possible route to complex **7c** were carried out. Reaction of **6c** with KPF_6 or direct reaction of **5** with $P[C_6H_3(OMe)_2]_3$ in the presence of KPF_6 gave **2c**. When **2c** was treated with NH_4Cl in acetone compound **7c** was obtained, whereas the reactions of **2a** or **2b** with NH_4Cl gave the corresponding starting compounds without any mononuclear complex. This reactivity difference is the result of the solubility differences of KCl and NH_4Cl formed initially in the acetone solution. The presence of water accelerated the metal–metal cleavage reaction.

A σ–σ* transition band appeared at 420, 427 and 432 nm for the dinuclear complexes **2a**, **2b** and **2c**, respectively. The metal–metal bond strength is assumed to decrease in this order. This trend is qualitatively in agreement with the increase in reactivity of the metal–metal bond. The triphenylphosphine complex **2d** with a stronger metal–metal bond [$\lambda_{max}(\sigma\text{–}\sigma^*) = 411$ nm] than those in **2a**–**2c** with high basicity did not react with NH_4Cl to give the starting dimeric compound quantitatively. The initial reaction is the formation of **6c**, followed by anion exchange with PF_6^- to give **2c**. Finally, compound **7c** was formed by the reaction of **2c** with the resultant NH_4Cl, as depicted in Scheme 3.

Spectroscopy

Spectral data are shown in Table 1. The σ–σ* transition band of the palladium dimers appeared at longer wavelength than that of the parent complex **1** (317 nm) and triphenylphosphine complex **2d**; the wavelength increased with the basicity of the phosphine ligands, $P[C_6H_3(OMe)_2]_3 > PPh[C_6H_3(OMe)_2]_2 > PPh_2[C_6H_3(OMe)_2] > PPh_3$. As also found for dinuclear cobalt carbonyl complexes[17] and dimeric isocyanide complexes of cobalt[18] and rhodium,[19] the spectral behaviour is the result of the accumulation of electron density on the metal–



Scheme 3 Possible route to complex **7c**; L = $P[C_6H_3(OMe)_2]_3$, R = 2,6-$Me_2C_6H_3$

Table 1 The σ–σ* transition and ^{31}P NMR spectral data for di- and tri-nuclear complexes in $CDCl_3$

Compound	$\lambda_{\sigma-\sigma^*}$/nm	$^{31}P(\delta)$
1 $[Pd_2(RNC)_6]^{2+}$	317	
$[Pd_2(RNC)_4(PPh_3)_2]^{2+}$	411	14.1
2a $[Pd_2(RNC)_4\{PPh_2[C_6H_3(OMe)_2]\}_2]^{2+}$	420	−2.71
2b $[Pd_2(RNC)_4\{PPh[C_6H_3(OMe)_2]_2\}_2]^{2+}$	427	−20.6[a]
2c $[Pd_2(RNC)_4\{P[C_6H_3(OMe)_2]_2\}_2]^{2+}$	432	−40.1[a]
4a $[Pt_2(RNC)_4\{PPh_2[C_6H_3(OMe)_2]\}_2]^{2+}$	322	16.9
4b $[Pt_2(RNC)_4\{PPh[C_6H_3(OMe)_2]_2\}_2]^{2+}$	326	2.29[a]
4c $[Pt_2(RNC)_4\{P[C_6H_3(OMe)_2]_3\}_2]^{2+}$	343	−17.2[a]
9a $[Pd_3(RNC)_6\{PPh_2[C_6H_3(OMe)_2]\}_2]^{2+}$	512[b]	0.14[a]
9b $[Pd_3(RNC)_6\{PPh[C_6H_3(OMe)_2]_2\}_2]^{2+}$	517[b]	−16.1[a]
11a $[Pt_3(RNC)_6\{PPh_2[C_6H_3(OMe)_2]\}_2]^{2+}$	—[c]	34.5
11b $[Pt_3(RNC)_6\{PPh[C_6H_3(OMe)_2]_2\}_2]^{2+}$	—[c]	21.7
11c $[Pt_3(RNC)_6\{P[C_6H_3(OMe)_2]_3\}_2]^{2+}$	—[c]	0.26

R = 2,6-$Me_2C_6H_3$. [a] Measured in $(CD_3)_2CO$. [b] Measured in MeOH. [c] An exact position was not confirmed.

Table 2 Selected bond lengths (Å) and angles (°) for $[PdCl(RNC)_2\{P[C_6H_3(OMe)_2]_3\}]PF_6$ **7c**

Pd–Cl	2.350(2)	Pd–C(1)	1.977(6)
Pd–C(2)	1.987(6)	C(1)–N(1)	1.139(5)
Pd–P(1)	2.292(2)	C(2)–N(2)	1.136(5)
Cl–Pd–P(1)	176.78(4)	Cl–Pd–C(1)	88.1(1)
Cl–Pd–C(2)	89.2(1)	P(1)–Pd–C(1)	95.1(1)
P(1)–Pd–C(2)	87.6(1)	C(1)–Pd–C(2)	176.4(2)
Pd–C(1)–N(1)	174.6(4)	Pd–C(2)–N(2)	178.1(4)
C(1)–N(1)–C(11)	173.6(4)	C(2)–N(2)–C(21)	177.8(4)
Pd···O(1)	3.313	Pd···O(4)	5.093
Pd···O(2)	5.053	Pd···O(5)	3.409
Pd···O(3)	2.799	Pd···O(6)	4.315

Table 3 Crystal data and experimental details for $[PdCl(RNC)_2\{P[C_6H_3(OMe)_2]_3\}]PF_6$ **7c**

Formula	$C_{42}H_{45}ClF_6N_2O_6P_2Pd$
M	991.62
Colour	Pale yellow
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	14.186(5)
b/Å	15.888(8)
c/Å	11.117(6)
α/°	103.49(5)
β/°	102.04(4)
γ/°	69.62(3)
U/Å^3	2262(4)
Z	2
D_c/g cm^{-3}	1.459
μ/cm^{-1}	6.02
No. unique data	7959
No. observations	6195 [$I > 3.0\sigma(I)$]
No. variables	541
F(000)	1012
R, R'	0.042, 0.052
Goodness of fit	2.03
Maximum shift/error	0.01

$R = \Sigma||F_o| - |F_c||/|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(F_o)$.

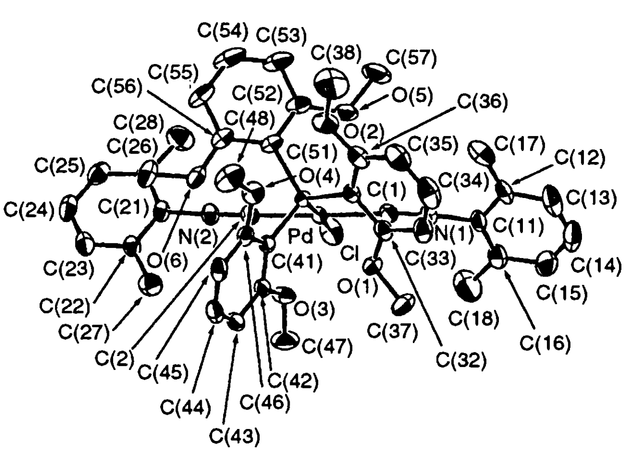


Fig. 1 Molecular structure of *trans*-$[PdCl(RNC)_2\{P[C_6H_3(OMe)_2]_3\}]PF_6$ **7c**

metal bond. The longest-wavelength band of the trinuclear palladium complexes appeared at longer wavelengths than those found for the dimeric complexes and increased with phosphine basicity, 512 nm for **9a** and 517 nm for **9b**.

Since for the platinum complexes the longest-wavelength band was observed as a shoulder an exact peak position could not be confirmed. However, the peaks appeared near 330 nm for the dimeric complexes **4** and near 470 nm for the trinuclear complexes. The absorption positions of the platinum complexes were observed at shorter wavelengths than those of the corresponding palladium analogues. This suggests that the metal–metal bond of the platinum complexes is stronger than that of the palladium analogues.

In extended Hückel molecular orbital (EHMO) calculations of $[Pt_nL_{2n+2}]^{2+}$ (L = HNC or CO) the energies of the highest occupied molecular orbitals (HOMOs) increased with the number of metals and those of its lowest unoccupied molecular orbitals (LUMOs) remained nearly almost unchanged. Thus, this result led to a decrease in the HOMO–LUMO band gap with an increase in the number of metals. The spectral behaviour is correlated to the extent of the band gap.

The ^{31}P-{^1H} chemical shifts of the platinum complexes were observed at lower magnetic field than those of the palladium complexes. This suggested that the σ donation from the

Table 4 Positional parameters of complex **7c**

Atom	*x*	*y*	*z*
Pd	0.202 25(2)	0.348 07(2)	0.217 88(3)
Cl	0.139 5(1)	0.437 0(1)	0.402 0(1)
P(1)	0.270 68(7)	0.264 84(7)	0.040 7(1)
P(2)	0.740 9(1)	0.090 8(1)	0.578 0(1)
F(1)	0.800 4(4)	0.162 3(4)	0.598 3(5)
F(2)	0.677 3(5)	0.027 9(4)	0.560 4(6)
F(3)	0.738 9(4)	0.077 8(4)	0.435 4(4)
F(4)	0.638 4(4)	0.172 4(3)	0.562 6(5)
F(5)	0.833 0(4)	0.007 7(4)	0.590 8(5)
F(6)	0.739 5(5)	0.111 1(4)	0.719 9(4)
O(1)	0.219 5(2)	0.131 0(2)	0.111 8(3)
O(2)	0.209 6(3)	0.240 7(3)	−0.246 2(3)
O(3)	0.373 4(2)	0.205 4(2)	0.287 7(3)
O(4)	0.415 8(2)	0.168 6(2)	−0.129 3(3)
O(5)	0.093 7(2)	0.384 9(2)	−0.077 0(3)
O(6)	0.443 5(3)	0.334 2(2)	0.026 0(3)
N(1)	0.011 5(3)	0.284 5(3)	0.164 2(3)
N(2)	0.382 9(3)	0.428 0(2)	0.288 1(3)
C(1)	0.081 5(3)	0.307 0(3)	0.177 6(4)
C(2)	0.318 5(3)	0.397 4(3)	0.262 1(4)
C(11)	−0.068 1(3)	0.249 1(3)	0.155 4(5)
C(12)	−0.121 4(3)	0.230 4(3)	0.036 5(5)
C(13)	−0.197 1(4)	0.192 1(4)	0.032 8(7)
C(14)	−0.216 8(5)	0.175 9(5)	0.136(1)
C(15)	−0.164 2(5)	0.194 9(5)	0.250 5(8)
C(16)	−0.086 7(4)	0.233 9(4)	0.263 8(6)
C(17)	−0.100 9(4)	0.252 0(4)	−0.074 3(6)
C(18)	−0.026 9(6)	0.255 8(7)	0.387 0(7)
C(21)	0.460 0(3)	0.469 0(3)	0.318 9(4)
C(22)	0.558 6(3)	0.415 5(3)	0.356 7(4)
C(23)	0.631 9(3)	0.459 9(4)	0.391 5(4)
C(24)	0.606 5(4)	0.551 2(4)	0.386 9(5)
C(25)	0.510 0(5)	0.600 3(4)	0.347 5(5)
C(26)	0.431 9(4)	0.561 3(3)	0.312 3(4)
C(27)	0.583 4(4)	0.316 9(4)	0.359 1(5)
C(28)	0.326 5(5)	0.613 1(4)	0.270 5(6)
C(31)	0.206 9(3)	0.189 1(3)	−0.065 8(4)
C(32)	0.185 7(3)	0.127 4(3)	−0.012 0(5)
C(33)	0.135 8(4)	0.066 6(3)	−0.084 6(6)
C(34)	0.110 2(5)	0.067 7(4)	−0.209 2(7)
C(35)	0.133 1(5)	0.122 7(5)	−0.266 5(5)
C(36)	0.182 1(3)	0.184 3(3)	−0.195 8(4)
C(37)	0.199 5(4)	0.072 9(4)	0.177 9(6)
C(38)	0.182 3(6)	0.243 5(7)	−0.376 2(5)
C(41)	0.397 1(3)	0.188 1(3)	0.079 3(4)
C(42)	0.434 1(3)	0.164 0(3)	0.197 6(4)
C(43)	0.530 5(3)	0.101 7(3)	0.220 8(5)
C(44)	0.588 1(3)	0.062 6(3)	0.125 1(6)
C(45)	0.554 9(3)	0.083 1(3)	0.007 2(5)
C(46)	0.458 5(3)	0.144 3(3)	−0.016 4(4)
C(47)	0.401 8(5)	0.177 4(4)	0.405 9(5)
C(48)	0.473 6(5)	0.137 3(4)	−0.229 4(6)
C(51)	0.269 1(3)	0.356 6(3)	−0.033 6(4)
C(52)	0.175 8(4)	0.409 3(3)	−0.085 1(4)
C(53)	0.165 7(5)	0.483 7(4)	−0.138 7(6)
C(54)	0.252 4(6)	0.504 1(4)	−0.138 0(6)
C(55)	0.345 2(5)	0.456 1(4)	−0.085 1(6)
C(56)	0.354 4(4)	0.382 3(3)	−0.032 2(4)
C(57)	0.000 3(4)	0.420 3(5)	−0.153 6(6)
C(58)	0.536 2(4)	0.344 4(4)	0.012 6(6)

phosphine ligands to the platinum atoms is stronger than that to the palladium. High σ donation to the platinum atoms is traced back to the back bonding from the metal to the isocyanide ligands, the ν(N≡C) stretching frequencies of the platinum complexes being at *ca.* 2152 $\mathrm{cm^{-1}}$ and those of the palladium ones at *ca.* 2160 $\mathrm{cm^{-1}}$. The $^{31}\mathrm{P}\text{-}\{^{1}\mathrm{H}\}$ chemical shifts of the dinuclear complexes appeared at higher magnetic field than those of the trinuclear complexes. In the infrared spectra the ν(N≡C) band of the trinuclear complexes appeared 20–30 $\mathrm{cm^{-1}}$ lower than those of the dimeric complexes. The $^{31}\mathrm{P}\text{-}\{^{1}\mathrm{H}\}$ NMR behaviour may be due mainly to the number of isocyanide ligands as electron acceptors rather than to a difference in oxidation states.

Crystal structure of complex 7c

The molecule is square planar and two isocyanide ligands are located in *trans* positions (Fig. 1). Selected bond lengths and angles are listed in Table 2. The Cl–Pd–P(1) and C(1)–Pd–C(2) bond angles are not significantly different from linearity. The *ipso*-carbon atom C(31) of one phenyl group attached to the P atom lies in the same plane as the $\mathrm{PdPC_2Cl}$ square plane. Two other *ipso*-carbon atoms lie symmetrically above and below the square plane. The P(1)–Pd–C(1) bond angle of 95.1(1)° is wider than three other bond angles [87.7(2)–89.1(2)°], minimizing repulsive interaction between the isocyanide [containing C(1)] and one of the 2,6-dimethoxyphenyl rings. In the distorted octahedral palladium complex $[\mathrm{Pd\{P[C_6H_2(OMe)_2]_3\}_2}][\mathrm{BF_4}]_2$ **13** the phosphine ligands are co-ordinated in a triphapto mode, (P,OMe,OMe). The average $\mathrm{Pd{-}O_{eq}}$ (ether oxygen) bond distance in the equatorial arrangement is 2.186(8) Å and the average $\mathrm{Pd{-}O_{ax}}$ length in the axial sites is 2.651(7) Å.[4] The Pd • • • O distances in **7c** are 2.799, 3.313 and 3.409 Å for O(3), O(1) and O(5), respectively. Even the shortest distance is well outside the expected range for covalent bonding. It is considered that a driving force for the octahedral geometry in compound **13** is the initial co-ordination of the ether-O groups at two equatorial positions. This (P and ether-O) co-ordination restricts the freedom of the phosphine ligands to enforce further axial co-ordination by other ether-O groups. Since two equatorial co-ordination sites are blocked by isocyanide ligands having stronger co-ordination ability than that of the ether O, the freedom of $\mathrm{P[C_6H_3(OMe)_2]_3}$ is maintained and it thus acts as a monohapto ligand in complex **7c**.

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