

Di- and tri-nuclear molybdenum–palladium complexes bearing strong π -acceptor “P–N–P” ligands, $\text{MeN}\{\text{P}(\text{OR})_2\}_2$ ($\text{R} = \text{CH}_2\text{CF}_3$ or Ph) [☆]

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Abstract

The dipalladium complexes, $[\text{PdCl}(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)]_2$ ($\text{R} = \text{CH}_2\text{CF}_3$, **1a**; Ph, **1b**) react with $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ in boiling benzene to afford the molybdenum–palladium heterometallic complexes, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)_2\text{PdCl}]$ ($\text{R} = \text{CH}_2\text{CF}_3$, **3a**; Ph, **3b**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_3\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)_2\text{Pd}_2\text{Cl}]$ ($\text{R} = \text{CH}_2\text{CF}_3$, **5a**; Ph, **5b**), $[(\eta^5\text{-C}_5\text{H}_5)(\text{Cl})\text{Mo}(\mu_2\text{-CO})(\mu_2\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)_2\text{PdCl}]$ ($\text{R} = \text{CH}_2\text{CF}_3$, **6a**; Ph, **6b**) and also the mononuclear complex $[\text{Mo}(\text{CO})\text{Cl}(\eta^5\text{-C}_5\text{H}_5)(\kappa^2\text{-MeN}\{\text{P}(\text{OR})_2\}_2)]$ ($\text{R} = \text{Ph}$, **4b**). These complexes have been separated by column chromatography and are characterised by elemental analysis, IR, ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR data. The structures of **1a**, **3a**, **4b**, **5b** and **6a** have been confirmed by single crystal X-ray diffraction. The CO ligands in **5b** and **6a** adopt a semi-bridging mode of bonding; the Mo–CO distances (1.95–1.97 Å) are shorter than the Pd–CO distances (2.40–2.48 Å). The Pd–Mo distances fall in the range, 2.63–2.86 Å. The reaction of $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ with $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$ in toluene gives $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\kappa^1\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ (**2**) in which the diphosphazane acts as a monodentate ligand.

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1. Introduction

Heterometallic complexes containing carbon monoxide and phosphane ligands have attracted considerable attention in recent years owing to their propensity to promote cooperative activation of substrates and exhibit site-specific reactivities as catalysts [1,2]. As a part of our research program on the organometallic chemistry of diphosphazane ligands based on the “P–N–P” framework [3], we report in this paper the synthesis and structural characterization of dipalladium, dimolybdenum and heterometallic palladium–molybdenum complexes bearing strong π -acceptor diphosphazane ligands $\text{MeN}\{\text{P}(\text{OR})_2\}_2$ ($\text{R} = \text{CH}_2\text{CF}_3$ or Ph) [4]. Several het-

erometallic complexes (Fe–Co, Fe–Rh, Fe–Ir, Mo–Ni, Mo–Pt, Mo–Rh and Mo–Ir) of the diphosphazane ligand $\text{MeN}(\text{PF}_2)_2$ have been reported by Mague and coworker [5]. Braunstein and coworkers [6] have synthesized palladium–cobalt, palladium–molybdenum and platinum–cobalt trinuclear clusters of diphosphazane ligands, $\text{RN}(\text{PPh}_2)_2$ [$\text{R} = \text{H}$, Me or $(\text{CH}_2)_3\text{Si}(\text{OEt})_3$].

2. Experimental

2.1. Materials and physical measurements

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker ACF – 200 or a Bruker AMX-400 spectrometer with Me_4Si as an internal standard for ^1H NMR measurements and 85% H_3PO_4 as an external standard for ^{31}P NMR measurements. Chemical shifts

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downfield from the standard were assigned positive values. Infrared spectra were recorded using a BIO-RAD FTIR Model FTS-7 or a Perkin–Elmer Model 457 spectrometer. The ligands, $\text{MeN}\{\text{P}(\text{OR})_2\}_2$ ($\text{R} = \text{CH}_2\text{CF}_3$ or Ph) [7] and the metal precursors, $[\text{PdCl}(\text{MeN}\{\text{P}(\text{OR})_2\}_2)]_2$ ($\text{R} = \text{Ph}$) [8], $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ [9] and $[\text{PdCl}_2(\text{COD})]$ [10] were prepared as reported previously.

2.2. The reactions of $[\text{Pd}(\text{COD})\text{Cl}_2]$ with $\text{MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2$

2.2.1. Synthesis of $[\text{Pd}_2\text{Cl}_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2]$ (**1a**)

A solution of $[\text{Pd}(\text{COD})\text{Cl}_2]$ (0.143 g, 0.50 mmol) and $\text{MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2$ (0.488 g, 1.00 mmol) in 25 ml of CH_2Cl_2 was stirred for 3 h. The solution was filtered and the filtrate concentrated to 8 ml. Addition of 8 ml of petrol followed by cooling at -15°C gave orange crystals of **1a**. Yield: 275 mg (86.0%). Anal. Calc. for $\text{C}_{18}\text{Cl}_2\text{F}_{24}\text{H}_{22}\text{N}_2\text{O}_8\text{P}_4\text{Pd}_2$: C, 17.2; H, 1.8; N, 2.2. Found: C, 17.1; H, 1.9; N, 2.2%. ^1H NMR (200 MHz, CDCl_3 , 25°C): δ 2.82 (m, 6H, NMe), 4.54–4.73 (m, 16H, CH_2 of OCH_2CF_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3 , 25°C): δ 120.0 (s).

2.2.2. Synthesis of $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_4(\kappa^1\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ (**2**)

A solution of $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ (0.095 g, 0.19 mmol) and $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$ (0.090 g, 0.19 mmol) in toluene (25 ml) was heated under reflux for 8 h. The solvent was evaporated and the residue extracted with diethyl ether. The extract was filtered to give a red solution, which was allowed to stand for 12 h to give dark green micro crystals of **2**. Yield: 66 mg (25.0%). Anal. Calc. for $\text{C}_{64}\text{H}_{56}\text{Mo}_2\text{N}_2\text{O}_{12}\text{P}_4$: C, 56.5; H, 4.1; N, 2.1. Found: C, 55.0; H, 4.4; N, 2.2%. IR (Neat, cm^{-1}): $\nu(\text{CO})$ 1898 (s), 1978 (s). ^1H NMR: δ 2.70 (dd, $^3J_{\text{HP}} = 5.6$ Hz, 6H, NMe), 4.90 (s, 10H, C_5H_5), 7.0–7.4 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 179.6 (d, $^2J_{\text{PP}} = 32.7$ Hz, P–Mo), 112.1 (d, $^2J_{\text{PP}} = 32.7$ Hz, P (dangling)).

2.2.3. Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{PdCl}]$ (**3a**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_{3\text{sb}}\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5a**), and $[(\eta^5\text{-C}_5\text{H}_5)\text{ClMo}(\mu_{\text{sb}}\text{-CO})(\mu\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{PdCl}]$ (**6a**)

A solution of $[\text{Pd}_2\text{Cl}_2(\text{MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2]$ (0.100 g, 0.080 mmol) and $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ (0.038 g, 0.077 mmol) in 40 ml of C_6H_6 was heated under reflux for 4 days using an oil bath maintained at 90°C . The reaction mixture was cooled to 25°C and the solvent removed in vacuum. The residue was dissolved in CH_2Cl_2 (6 ml) and subjected to chromatography using a column of dimensions 50 cm length and 1.5 cm inner diameter packed with 50 g of silica gel. Successive elutions with

petrol–dichloromethane (1:1), dichloromethane and dichloromethane–ethyl acetate (2:1) gave red, green and orange coloured fractions, respectively. The solvent was removed from each fraction in vacuum to obtain the complexes **3a**, **5a** and **6a**, respectively. Single crystals of **3a** suitable for X-ray diffraction studies were obtained from diethylether at -15°C ; single crystals of **6a** were obtained by fractional crystallization of the reaction mixture from CH_2Cl_2 –petrol (1:2 v/v) at -15°C . When the reaction was carried out with a 1:2 stoichiometric ratio of the starting dipalladium and dimolybdenum complexes and the reaction mixture subjected to column chromatography, initial elution with petrol–dichloromethane (3:1) gave an orange coloured fraction from which solvent was removed to obtain a solid residue. The ^{31}P NMR spectrum of this product showed two singlets at δ 168.0 and 181.8. The nature of the product could not be ascertained. Complexes **3a**, **5a** and **6a** were also isolated from this reaction as described above.

2.2.4. Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ (**3b**), $[\text{Mo}(\text{CO})\text{Cl}(\eta^5\text{-C}_5\text{H}_5)(\kappa^2\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)]$ (**4b**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_{3\text{sb}}\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5b**) and $[(\eta^5\text{-C}_5\text{H}_5)\text{ClMo}(\mu_{\text{sb}}\text{-CO})(\mu\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{PdCl}]$ (**6b**)

A solution of $[\text{Pd}_2\text{Cl}_2(\text{MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ (0.100 g, 0.083 mmol) and $[\text{Mo}_2\text{Cp}_2(\text{CO})_6]$ (0.045 g, 0.092 mmol) in 40 ml benzene was heated under reflux for 3 days using an oil bath maintained at 90°C . The reaction mixture was cooled to 25°C and the solvent removed in vacuum. The residue was dissolved in 6 ml of dichloromethane and loaded on top of a silica gel column. Successive elutions with petrol–diethyl ether, 4:1, 2:1 and 1:1 v/v mixtures gave pink, orange and green fractions, respectively. The solvent was removed from each fraction under reduced pressure to obtain the complexes **3b**, **4b** and **5b**, respectively. Further elution with diethylether–dichloromethane (4:1) gave an orange fraction from which the solvent was removed in vacuum to isolate **6b**; this was recrystallized from CH_2Cl_2 /petrol (1:2) at -15°C . Single crystals of **4b** and **5b** suitable for X-ray diffraction studies were obtained from CH_2Cl_2 /petrol (1:3 v/v) and CH_2Cl_2 /petrol/diethylether (1:1:2 v/v) at -15°C , respectively.

The yields (based on Mo), analytical and spectroscopic data for the complexes are given below.

2.2.5. $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{PdCl}]$ (**3a**)

Yield: 57 mg, 28.4%. Anal. Calc. for $\text{C}_{24}\text{ClF}_{24}\text{H}_{27}\text{MoN}_2\text{O}_9\text{P}_4\text{Pd}$: C, 22.1; H, 2.1; N, 2.2. Found: C, 22.2; H, 2.1; N, 2.2%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1863 (s). ^1H NMR: δ 2.83 (m, 6H, NMe), 4.04–4.90 (m, 16H, CH_2 of OCH_2CF_3), 5.28 (d, $^3J_{\text{HP}} = 3.8$ Hz, 5H, C_5H_5).

Table 1
Details of the X-ray data collection, structure solution and refinement for compounds **1a**, **3a**, **4b**, **5b** and **6a**

	1a	3a	4b · CH ₂ Cl ₂	5b · 0.5CH ₂ Cl ₂	6a
Empirical formula	C ₁₈ Cl ₂ F ₂₄ H ₂₂ , N ₂ O ₈ P ₄ Pd ₂	C ₂₄ ClF ₂₄ H ₂₇ MoN ₂ O ₉ P ₄ Pd	C ₃₁ ClH ₂₈ MoNO ₅ P ₂ · CH ₂ Cl ₂	C ₅₇ ClH ₅₁ MoN ₂ O ₁₀ P ₄ Pd ₂ · 0.5CH ₂ Cl ₂	C ₁₅ Cl ₃ F ₁₂ H ₁₆ MoNO ₅ P ₂ Pd
Formula weight	1257.9	1305.15	772.80	1435.54	888.92
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.067(1)	12.058(1)	10.262(6)	11.946(8)	14.537(7)
<i>b</i> (Å)	9.759(1)	18.203(4)	12.554(2)	21.09(2)	19.163(2)
<i>c</i> (Å)	11.882(1)	21.481(1)	14.864(2)	23.757(7)	21.363(4)
α (°)	82.79(1)	90.00	106.45(2)	96.62(4)	90.00
β (°)	80.57(1)	106.158(9)	104.24(2)	99.19(4)	108.18(3)
γ (°)	82.65(1)	90.00	103.29(3)	89.84(6)	90.00
Volume (Å ³)	1022.8(2)	4528.9(1)	1685.2(1)	5867.9(6)	5654.1(3)
<i>Z</i>	1	4	2	4	8
<i>D</i> _C (mg m ⁻³)	2.042	1.914	1.523	1.625	2.089
μ (Mo K α) (mm ⁻¹)	1.317	1.019	0.762	1.075	1.584
<i>F</i> (0 0 0)	610	2552	784	2876	3440
Crystal size (mm)	0.8 × 0.5 × 0.15	0.8 × 0.6 × 0.13	0.19 × 0.14 × 0.140	0.8 × 0.8 × 0.12	0.7 × 0.4 × 0.11
θ Ranges (°)	1.75–30.44	1.49–24.97	1.52–24.96	1.23–24.98	1.46–24.98
<i>h, k, l</i> Ranges	0 ≤ <i>h</i> ≤ 10, −11 ≤ <i>k</i> ≤ 11, −14 ≤ <i>l</i> ≤ 14	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 21, −25 ≤ <i>l</i> ≤ 24	0 ≤ <i>h</i> ≤ 12, −14 ≤ <i>k</i> ≤ 14, −17 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 14, −25 ≤ <i>k</i> ≤ 25, −28 ≤ <i>l</i> ≤ 27	0 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 22, −25 ≤ <i>l</i> ≤ 24
Reflections collected	3833	8980	6313	24,194	10,450
Independent reflections (<i>R</i> _{int})	3585 (0.0093)	7956 (0.0345)	5908 (0.0199)	20,580 (0.0208)	9939 (0.0499)
Data/restraints/parameters	3584/90/267	7944/225/583	5907/0/397	20,544/0/1413	9915/180/711
Goodness-of-fit on <i>F</i> ²	0.982	1.076	0.862	1.067	1.059
Final <i>R</i> indices [<i>I</i> < 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0500, <i>wR</i> ₂ = 0.1469	<i>R</i> ₁ = 0.0700, <i>wR</i> ₂ = 0.1775	<i>R</i> ₁ = 0.0440, <i>wR</i> ₂ = 0.1190	<i>R</i> ₁ = 0.0937, <i>wR</i> ₂ = 0.2213	<i>R</i> ₁ = 0.0676, <i>wR</i> ₂ = 0.1411
<i>R</i> indices ^{a,b} (all data)	<i>R</i> ₁ = 0.0552, <i>wR</i> ₂ = 0.1551	<i>R</i> ₁ = 0.1213, <i>wR</i> ₂ = 0.2248	<i>R</i> ₁ = 0.0497, <i>wR</i> ₂ = 0.1283	<i>R</i> ₁ = 0.1549, <i>wR</i> ₂ = 0.2855	<i>R</i> ₁ = 0.1433, <i>wR</i> ₂ = 0.1932
Largest difference peak and hole (e Å ⁻³)	0.946 and −0.918	0.791 and −0.649	1.131 and −1.314	1.869 and −2.342	0.890 and −0.716

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_c|$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$$

$$w = 1/[\sigma^2(F_o^2) + (0.1001 \times p)^2 + 3.3972 \times p] \text{ where } p = (\text{Max}(F_o^2, 0) + 2 \times F_o^2)/3 \text{ for complex } \mathbf{1a}.$$

$$w = 1/[\sigma^2(F_o^2) + (0.1084 \times p)^2 + 15.8530 \times p] \text{ where } p = (\text{Max}(F_o^2, 0) + 2 \times F_o^2)/3 \text{ for complex } \mathbf{3a}.$$

$$w = 1/[\sigma^2(F_o^2) + (0.1065 \times p)^2 + 2.6045 \times p] \text{ where } p = (\text{Max}(F_o^2, 0) + 2 \times F_o^2)/3 \text{ for complex } \mathbf{4b}.$$

$$w = 1/[\sigma^2(F_o^2) + (0.1449 \times p)^2 + 53.3663 \times p] \text{ where } p = (\text{Max}(F_o^2, 0) + 2 \times F_o^2)/3 \text{ for complex } \mathbf{5b}.$$

$$w = 1/[\sigma^2(F_o^2) + (0.0718 \times p)^2 + 38.6963 \times p] \text{ where } p = (\text{Max}(F_o^2, 0) + 2 \times F_o^2)/3 \text{ for complex } \mathbf{6a}.$$

2.2.6. $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{PdCl}]$ (**3b**)

Yield: 5 mg, 2.2%. This compound was formed in low yield (<5%) and could not be obtained in a pure state. It was only identified from ^{31}P NMR data (Table 3).

2.2.7. $[\text{Mo}(\text{CO})\text{Cl}(\eta^5\text{-C}_5\text{H}_5)(\kappa^2\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)]$ (**4b**) $\cdot \text{CH}_2\text{Cl}_2$

Yield: 36 mg, 26.2%. Anal. Calc. for $\text{C}_{32}\text{Cl}_3\text{H}_{30}\text{MoNO}_5\text{P}_2$: C, 49.7; H, 3.9; N, 1.8. Found: C, 49.1; H, 3.7; N, 1.7%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1880 (s). ^1H NMR: δ 2.61 (dd, $^3J_{\text{HP}} = 12, 10$ Hz, 3H, NMe), 4.83 (d, $^3J_{\text{HP}} = 2.6$ Hz, 5H, C_5H_5), 5.3 (s, 2H, solvated CH_2Cl_2), 6.6–7.5 (m, 20H, Ph).

2.2.8. $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_{3sb}\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5a**)

Yield: 58 mg, 26.1%. Anal. Calc. for $\text{C}_{25}\text{ClF}_{24}\text{H}_{27}\text{MoN}_2\text{O}_{10}\text{P}_4\text{Pd}_2$: C, 20.8; H, 1.9; N, 1.9. Found: C, 20.4; H, 1.6; N, 1.8%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1815. ^1H NMR: δ 2.72 (t, $^3J_{\text{HP}} = 6.5$ Hz, 3H, NMe), 2.86 (t, $^3J_{\text{HP}} = 6.7$ Hz, 3H, NMe), 3.87–5.01 (m, 16H, CH_2 of OCH_2CF_3), 5.33 (s, 5H, C_5H_5).

2.2.9. $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_{3sb}\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5b**) $\cdot 0.5\text{CH}_2\text{Cl}_2$

Yield: 65 mg, 24.6%. Anal. Calc. for $\text{C}_{57.5}\text{Cl}_2\text{H}_{52}\text{MoN}_2\text{O}_{10}\text{P}_4\text{Pd}_2$: C, 48.1; H, 3.7; N, 1.9. Found: C, 48.5; H, 3.4; N, 1.9%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1795 (s). ^1H NMR: δ 2.53 (t, $^3J_{\text{HP}} = 6.7$ Hz, 3H, NMe), 2.81 (t, $^3J_{\text{HP}} = 6.4$ Hz, 3H, NMe), 4.50 (s, 5H, C_5H_5), 5.3 (s, 2H, solvated CH_2Cl_2), 6.8–7.6 (m, 40H, Ph).

2.2.10. $[(\eta^5\text{-C}_5\text{H}_5)\text{ClMo}(\mu_{sb}\text{-CO})(\mu\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{PdCl}]$ (**6a**)

Yield: 30 mg, 21.9%. Anal. Calc. for $\text{C}_{15}\text{Cl}_3\text{F}_{12}\text{H}_{16}\text{MoNO}_5\text{P}_2\text{Pd}$: C, 20.3; H, 1.8; N, 1.6. Found: C, 19.9; H, 1.9; N, 1.55%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1935. ^1H NMR: δ 2.96 (t, $^3J_{\text{HP}} = 7.5$ Hz, 3H, NMe), 4.3–5.2 (m, 8H, CH_2 of OCH_2CF_3), 5.70 (d, $^3J_{\text{HP}} = 2.8$ Hz, 5H, C_5H_5).

2.2.11. $[(\eta^5\text{-C}_5\text{H}_5)\text{ClMo}(\mu_{sb}\text{-CO})(\mu\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{PdCl}]$ (**6b**)

Yield: 8 mg, 5.0%. Anal. Calc. for $\text{C}_{31}\text{Cl}_3\text{H}_{28}\text{MoNO}_5\text{P}_2\text{Pd}$: C, 43.0; H, 3.2; N, 1.6. Found: C, 42.6; H, 3.0; N, 1.5%. IR (Nujol, cm^{-1}): $\nu(\text{CO})$ 1910. ^1H NMR: δ 3.15 (t, $^3J_{\text{HP}} = 7.6$ Hz, 3H, NMe), 5.26 (d, $^3J_{\text{HP}} = 2.6$ Hz, 5H, C_5H_5), 7.2–7.8 (m, 20H, Ph).

2.3. X-ray crystallography

The diffraction data for complexes **1a**, **3a**, **4b**, **5b** and **6a** were collected using a Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Details of the data collection and

refinements are given in Table 1. The structures were solved by conventional Patterson method using SHELXS-86 and refined by full-matrix least squares with SHELXL-93 [11]. All hydrogen atoms were included in the calculated positions [$\text{C-H} = 0.96\text{--}0.97$ Å] with a fixed isotropic displacement parameters except the disordered atoms. All non-hydrogen atoms were refined anisotropically except the disordered ones. In the structure of **1a**, disorder of fluorine atoms attached to C6 and C9 was observed. In the structure of **3a**, disorder of C16, C18, C24 and fluorines attached to C18, C19, C22, C23, and C24 was observed. In the structure of **6a**, disorder of C12 and C27 and the fluorine atoms attached to C12, C13, C27 and C29 was observed. In the structure of **5b**, disorder of the phenyl group and solvent (CH_2Cl_2) carbon atoms was observed. The refinements of these atoms were carried out using SADI option available in SHELXL-93 and stopped near convergence. The site occupancy factors are given in Section 5.

3. Results and discussion

3.1. Dinuclear palladium complex, $[\text{Pd}_2\text{Cl}_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2]$ (**1a**)

3.1.1. Synthesis, spectroscopic data and structure

The dipalladium complex **1a** can be isolated as the major product (86%) from the reaction of $[\text{PdCl}_2(\text{COD})]$ and $\text{MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2$ in CH_2Cl_2 by using 1:2 stoichiometry of the reactants and by crystallization of the reaction mixture from $\text{CH}_2\text{Cl}_2/\text{petrol}$ (1:1 v/v) [12]. An analogous reaction of $[\text{PdCl}_2(\text{COD})]$ with $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$ produces the dipalladium complex, $[\text{PdCl}(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ (**1b**) and the chelate complex, $[\text{PdCl}_2(\kappa^2\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)]$ as shown by the ^{31}P NMR spectrum of the reaction mixture. Dipalladium complexes of type **1a** and **1b** containing two bridging diphosphorus ligands are usually prepared by a disproportionation reaction between $\text{Pd}(\text{II})$ and $\text{Pd}(0)$ complexes [13]. Several studies have shown that $\text{Pd}(0)$ -phosphine complexes are formed by the reduction of divalent palladium in the presence of a monophosphine ligand [14–17] and adventitious water. In addition to water, a fluorinating agent such as NaBF_4 or AgF facilitates the reduction of $\text{Pd}(\text{II})$ when a diphosphine [18,19] {e.g., $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)} is used. The reduction of Pd^{2+} to Pd^0 to form the dinuclear complex **1a** occurs (evidently in the presence of adventitious water) without the need to use a reducing agent to bring about the reduction because of the strong π -acceptor ability of the diphosphazane ligands, $\text{MeN}\{\text{P}(\text{OR})_2\}_2$ ($\text{R} = \text{CH}_2\text{CF}_3$ or Ph) [7].

The ^1H NMR spectrum of **1a** shows a quintet pattern for the *N*-methyl protons which is a characteristic signal

for the presence of two diphosphazane ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a sharp singlet at δ 120.0 which lies upfield to the chemical shift for the ligand ($\delta_{\text{complex}} - \delta_{\text{ligand}} = -29.9$ ppm). The structure of **1a** is confirmed by single crystal X-ray diffraction. A perspective view of the molecule is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The molecule is centrosymmetric unlike the analogous phenyl derivative $[\text{Pd}_2\text{Cl}_2\{\text{PhN}(\text{P}(\text{OPh})_2)_2\}_2]$ [8]. The coordination geometry around palladium is distorted square planar. The Pd–Pd separation [2.629(1) Å] and the mean Pd–P distance [2.259(2) Å] lie in between those observed for the closely related dipalladium(I) complexes, $[\text{Pd}_2\text{Cl}_2\{\text{PhN}(\text{P}(\text{OPh})_2)_2\}_2]$ [8] and $[\text{Pd}_2\text{Cl}_2\{\text{HN}(\text{PPh}_2)_2\}_2]$ [20].

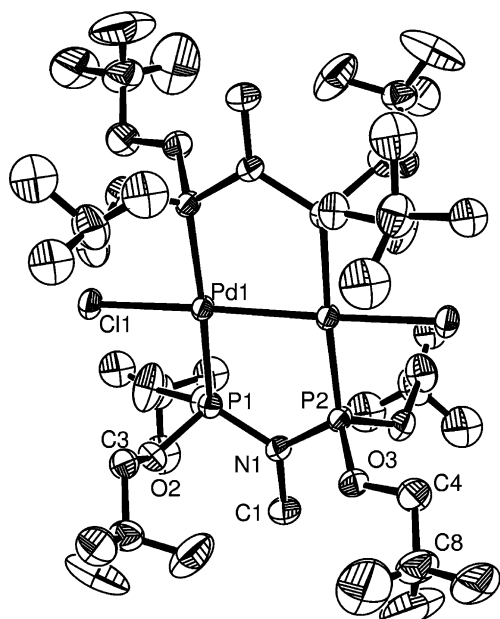


Fig. 1. The molecular structure of $[\text{Pd}_2\text{Cl}_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2]$ (**1a**).

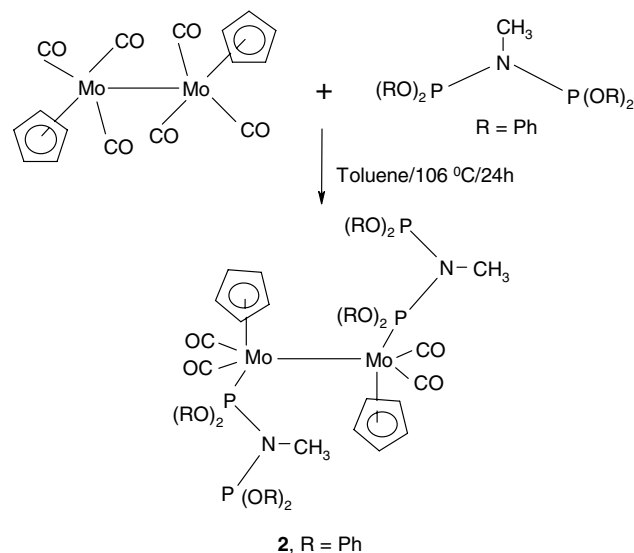
Table 2
Selected bond distances (Å) and bond angles (°) in **1a**

Pd(1)–Pd(1A)	2.629(1)
Pd(1)–P(1)	2.257(2)
Pd(1)–P(2A)	2.261(2)
Pd(1)–Cl(1)	2.395(2)
P(1)–N(1)	1.658(5)
P(2)–N(1)	1.656(5)
P(1)–Pd(1)–Cl(1)	87.7(1)
P(2A)–Pd(1)–Cl(1)	87.8(1)
P(1)–Pd(1)–Pd(1A)	92.0(1)
P(2A)–Pd(1)–Pd(1A)	92.6(1)
Cl(1)–Pd(1)–Pd(1A)	176.9(1)
P(1)–Pd(1)–P(2A)	174.6(1)
P(1)–N(1)–P(2)	116.2(3)

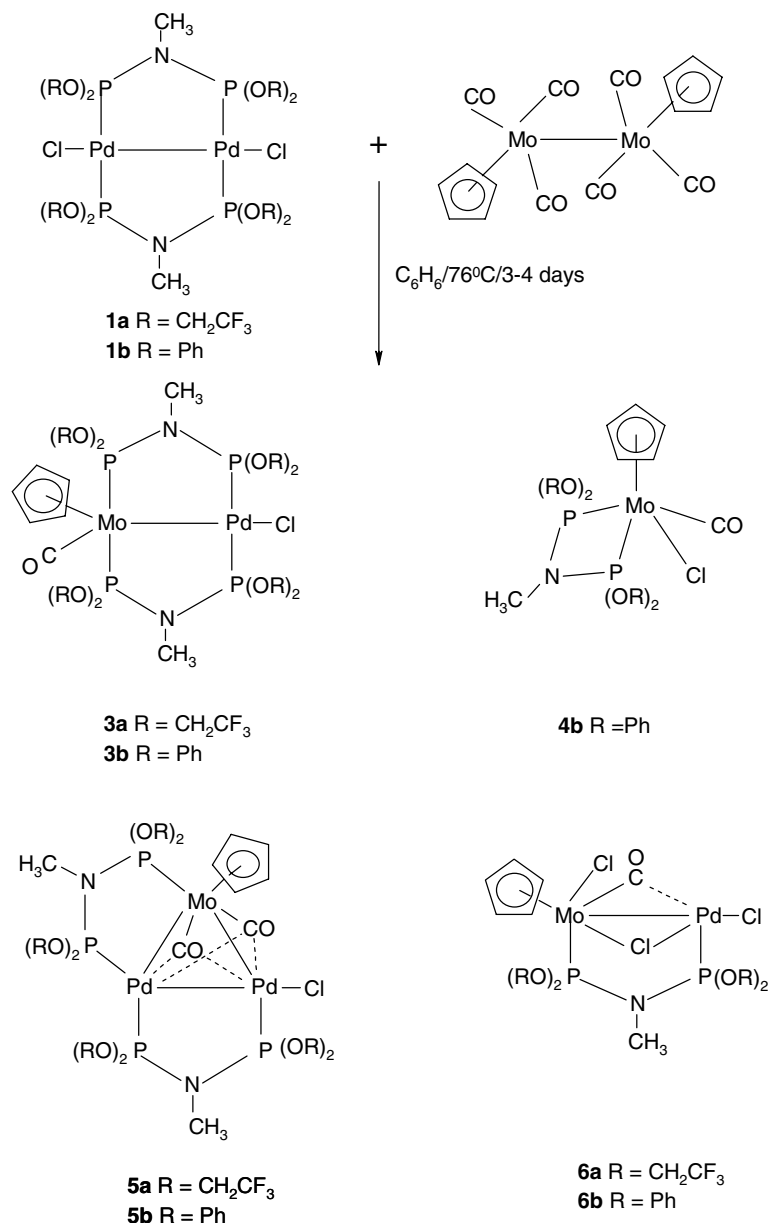
3.2. Reaction of $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ with $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$

The reaction between $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ and $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$ in boiling toluene affords the complex, $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\kappa^1\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2]$ **2** as dark green micro crystals. The compound is isolated by crystallization of the reaction mixture from diethyl ether (Scheme 1). Although the elemental analysis results give a slightly lower carbon percentage than the value expected for the above formula, the relative integrated intensities of the methyl, C_5H_5 and aryl proton resonances in the ^1H NMR spectrum support the above formula. A doublet of doublets is observed for the *N*-methyl protons at δ 2.70 indicating that the phosphorus nuclei are nonequivalent. The ^{31}P NMR spectrum shows two doublets centered at δ 179.6 and 112.1 ($^2J_{\text{PP}} = 32.7$ Hz) which can be assigned to the coordinated and uncoordinated phosphorus nuclei, respectively. Such a considerable deshielding of the coordinated phosphorus has also been noted for many molybdenum complexes containing κ^1 -coordinated $\text{MeN}(\text{PF}_2)_2$ ligand [21] and molybdenum carbonyl complexes of κ^1 -coordinated cyclodiphosphazanes [3a]. The IR spectrum of **2** shows strong peaks at 1898 and 1978 cm^{-1} which signify the presence of terminal carbonyl groups. A *cis* or *trans* orientation of the Cp (or diphosphazane) ligands is possible for compound **2** and a *trans*-structure is tentatively assigned to it.

The reaction of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6]$ with the diphosphazane, $\text{Pr}^i\text{N}(\text{PPh}_2)_2$ gives both a salt-like complex, $[(\eta^5\text{-C}_5\text{H}_5)\{\text{Pr}^i\text{N}(\text{PPh}_2)_2\}(\text{CO})_2\text{Mo}]^+[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Mo}]^-$ and diphosphazane bridged complex $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2\{\mu\text{-Pr}^i\text{N}(\text{PPh}_2)_2\}]$ [22]. The reaction of $\text{MeN}(\text{PF}_2)_2$ with $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4]$ gives the diphosphazane bridged complex $[\text{Mo}_2(\text{CO})_4(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-MeN}(\text{PF}_2)_2)]$ [5b]. In the present study, it is observed



Scheme 1.



Scheme 2.

that the reaction of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6]$ with $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$ gives the dimolybdenum complex **2** bearing two κ^1 -coordinated diphosphazane ligands as a result of pairwise substitution of the CO ligands by the strong π -acceptor diphosphazane ligand $\text{MeN}\{\text{P}(\text{OPh})_2\}_2$. This behavior is also observed in the reactions of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6]$ with phosphites such as $\text{P}(\text{O}i\text{Bu})_3$ or $\text{P}(\text{OPh})_3$ [23].

3.3. Molybdenum–palladium heterometallic complexes

3.3.1. Synthesis and spectroscopic data

Treatment of $[\text{Pd}_2\text{Cl}_2(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)_2]$ (R = CH₂CF₃) **1a** with an equimolar quantity of $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ in boiling benzene for 4 days gives

several products (Scheme 2). Three complexes, **3a**, **5a** and **6a** can be isolated in a pure form from the reaction mixture by column chromatography over silica gel. No definitive evidence could be obtained for the formation of the chelate complex $[\text{Mo}(\text{CO})\text{Cl}(\eta^5\text{-C}_5\text{H}_5)(\kappa^2\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)]$ analogous to **4b**. Treatment of an equimolar quantity of the phenoxy substituted diphosphazane complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-MeN}\{\text{P}(\text{OR})_2\}_2)_2]$ (R = Ph) **1b** with $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ yields the complexes **3b**, **4b**, **5b** and **6b** which are separated by column chromatography over silica gel (Scheme 2). The relative yields of the different complexes in the trifluoroethoxy (3a, 5a and 6a) and the phenoxy series (3b–6b) vary (see Section 2). The trifluoroethoxy substituted ligand prefers to form a bridging type of complex rather than

a chelate type of complex. There is no reaction between the dipalladium complex (**1a** or **1b**) and $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$ in toluene at 25 °C for 24 h; the dipalladium complex is recovered unchanged.

The structures of **3a**, **5a** and **6a** and **3b–6b** are deduced from their IR and NMR spectroscopic data and confirmed by single crystal X-ray diffraction studies for **3a**, **4b**, **5b** and **6a**. The ^{31}P NMR data are given in Table 3.

Both **3a** and **3b** represent examples of a 32-valence electron Mo–Pd heterometallic complex. Their ^{31}P NMR spectra are of the AA'XX' type. The low field resonances (XX' region) are assigned to the phosphorus nuclei attached to molybdenum and the high field resonances (AA' region) are assigned to the phosphorus nuclei attached to palladium. The analysis of the XX' region of the spectrum of **3a** yields the parameters shown in Table 3. The $J_{\text{AA}'}$ value (839.7 Hz) is much higher than that reported for the complex, $[\text{Pd}(\mu\text{-CO})(\mu\text{-dppm})_2\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]^+$ [24]. Such an analy-

sis could not be carried out for **3b** as the outer lines in the AA'XX' spectrum were not observed. The ^1H NMR spectrum of **3a** shows a quintet pattern for the methyl group attached to nitrogen consistent with presence of two diphosphazane ligands attached to the metal centers. The ^{31}P NMR spectrum of **4b** shows the expected AX spin pattern. The magnitude of $^2J_{\text{PP}}$ (43.7 Hz) is larger than that observed for the analogous $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe) complex, $[\text{CpMo}(\text{Cl})\text{CO}(\text{dppe})]$ [$^2J_{\text{PP}} = 38.0$ Hz] [25].

The complexes **5a** and **5b** represent examples of a 44-valence electron Mo–Pd trinuclear cluster and are similar to the dppm complex, $[\text{Pd}_2\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{Cl})(\mu_3\text{-CO})_2(\mu\text{-dppm})_2]$, which was prepared and structurally characterized by Braunstein et al. [26]. The IR spectra of **5a** and **5b** show a strong peak at 1815 and 1795 cm^{-1} , respectively, which can be ascribed to semi-bridging CO groups. The ^{31}P NMR spectra of **5a** and **5b** provide interesting examples of a four spin system in which all four phosphorus nuclei are magnetically

Table 3
The ^{31}P NMR data for heterometallic molybdenum–palladium complexes **3–6**^a

Complex	δ , $^{31}\text{P}\{-^1\text{H}\}$
3a	134.8 (m, P _A –Pd), 185.8 (m, P _X –Mo) ^b $J_{\text{AA}'} = 839.7$, $J_{\text{AX}} = J_{\text{A}'\text{X}'} = 174.2$ $J_{\text{AX}'} = J_{\text{A}'\text{X}} = 38.1$, $J_{\text{XX}'} = 31.1$
3b	130.4 (m, P–Pd), 176.7 (m, P–Mo) ^c
4b	143.2 (d, P–Mo), 153.7 (d, P–Mo) $^2J_{\text{PP}} = 43.7$
5a ^{d,e}	109.124 (ddd, P ₁ –Pd), 125.409 (ddd, P ₃ –Pd), 126.607 (ddd, P ₂ –Pd), 190.636 (ddd, P ₄ –Mo), $J_{1,2} = 70.4$, $J_{1,3} = 142.5$, $J_{1,4} = 201.6$, $J_{2,3} = 121.7$, $J_{2,4} = 49.0$, $J_{3,4} = 23.9$
5b ^e	88.2 (ddd, P ₁ –Pd), 110.5 (ddd, P ₃ –Pd), 112.8 (ddd, P ₂ –Pd), 178.2 (ddd, P ₄ –Mo), $J_{1,2} = 88.1$, $J_{1,3} = 157.3$, $J_{1,4} = 190.3$, $J_{2,3} = 118.9$, $J_{2,4} = 55.7$, $J_{3,4} = 38.7$
6a	123.9 (d, P–Pd), 154.0 (d, P–Mo) $^2J_{\text{PP}} = 117.5$
6b	108.3 (d, P–Pd), 151.0 (d, P–Mo) $^2J_{\text{PP}} = 114.7$

^a Recorded in CDCl_3 at 161.9 MHz, 25 °C, δ in ppm, J in Hz.

^b AA'XX' spectrum.

^c AA'XX' spectrum; outer lines could not be observed.

^d Recorded at 243 MHz.

^e For labeling of the P nuclei, see Fig. 2.

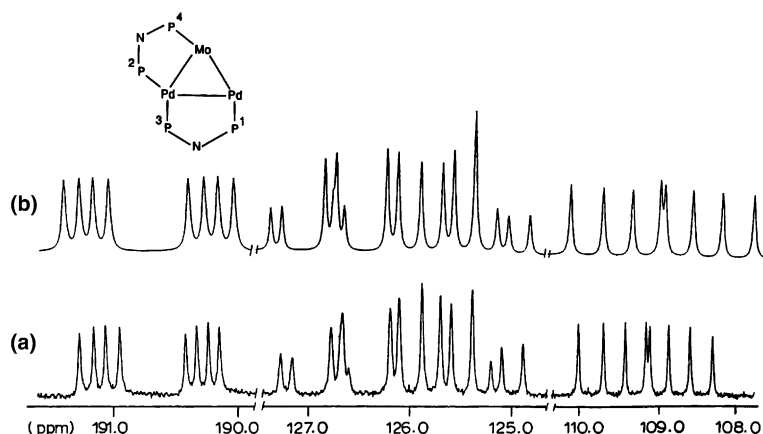


Fig. 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_3\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5a**): (a) experimental; (b) simulated.

nonequivalent and coupled to each other. The spectra have been analyzed by iterative computer simulation and the parameters are listed in Table 3. The experimental and the computer simulated spectra for **5a** are illustrated in Fig. 2. The assignment of the chemical shifts and consequently the coupling constants are tentative except the highly deshielded one which is assigned to the phosphorus attached to molybdenum. An AX type pattern is observed in the ^{31}P NMR spectra of the heterodinuclear complexes **6a** and **6b**. The IR spectra show strong peaks at 1935 and 1910 cm^{-1} for the semi-bridging CO groups. These values are considerably higher than those reported for $[\text{PdMo}(\mu\text{-Ph}_2\text{PPy})_2(\mu\text{-CO})(\text{CO})_2\text{Cl}_2]$ [27] and $[(\text{Cp})\text{Co}\{\mu,\eta^2\text{-P,O-P(O)(OMe)}_2\}_3\text{Mo}(\text{CO})(\mu,\eta^2\text{-C,N-C}(\text{C}_6\text{H}_4\text{Me-P})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)-(\mu\text{-CO})\text{PdI}]$ [28], containing semi-bridging CO groups. This is probably due to the formal higher oxidation state (+2.5) of molybdenum in **6a** and **6b**.

3.4. Crystal and molecular structures of **3a**, **4b**, **5b** and **6a**

The molecular structures of **3a**, **4b**, **5b** and **6a** as determined by single crystal X-ray diffraction studies are depicted in Figs. 3–6, respectively. Selected bond distances and bond angles are summarized in Tables 4–7.

The molecule of **3a** may be regarded as one derived from the Pd(I) dimer by the replacement of a 'Pd-Cl' unit by a 'CpMo(CO)' unit. Molybdenum and palladium are linked by two bridging diphosphazane ligands which are disposed nearly *trans* to each other. The coordination geometry around the Mo atom is that of a four legged piano stool (including M–M bond). The geome-

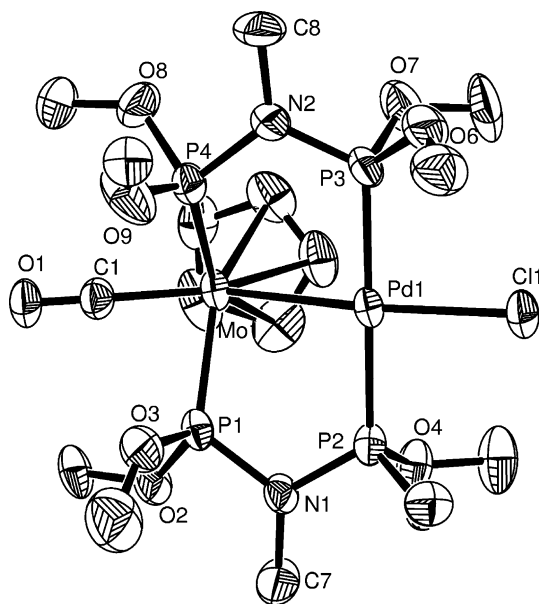


Fig. 3. The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)_2\text{PdCl}]$ (**3a**). The CF_3 groups have been omitted for clarity.

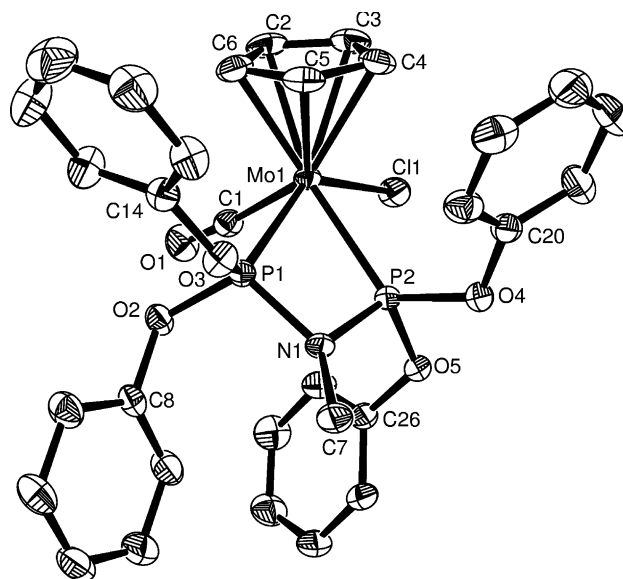


Fig. 4. The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})\text{Cl}(\kappa^2\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)]$ (**4b**).

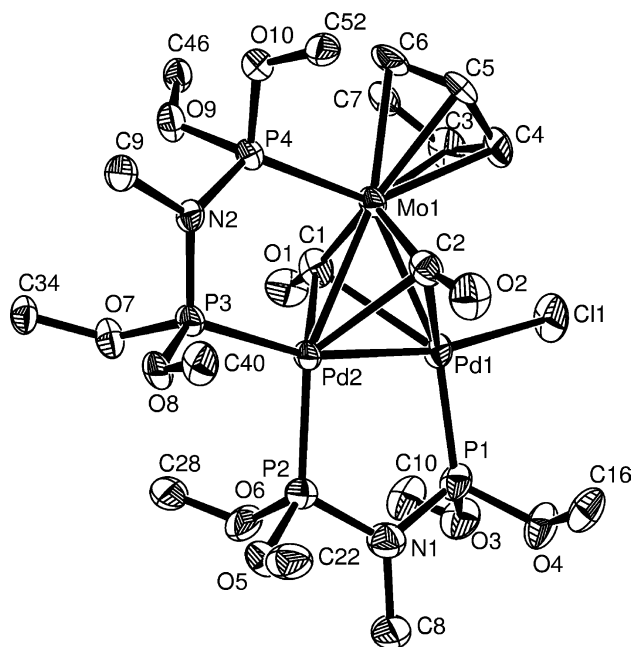


Fig. 5. The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu_3\text{-CO})_2(\mu\text{-MeN}\{\text{P}(\text{OPh})_2\}_2)_2\text{Pd}_2\text{Cl}]$ (**5b**). For clarity only the *ipso* carbons of the phenyl rings are shown.

try around the Pd atom is distorted square planar. The molecule adopts a partially staggered configuration; the torsion angles of $\text{P}(2)\text{-Pd}(1)\text{-Mo}(1)\text{-P}(1)$ and $\text{P}(3)\text{-Pd}(1)\text{-Mo}(1)\text{-P}(4)$ are $28.1(1)^\circ$ and $-31.1(1)^\circ$, respectively. The $\text{P}(1)\text{-Mo}(1)\text{-P}(4)$ angle [$118.7(1)^\circ$] deviates from collinearity compared to $\text{P}(2)\text{-Pd}(1)\text{-P}(3)$ angle [$179.3(1)^\circ$] owing to the presence of the cyclopentadienyl ligand at molybdenum. The Mo–Pd distance [$2.860(1)$

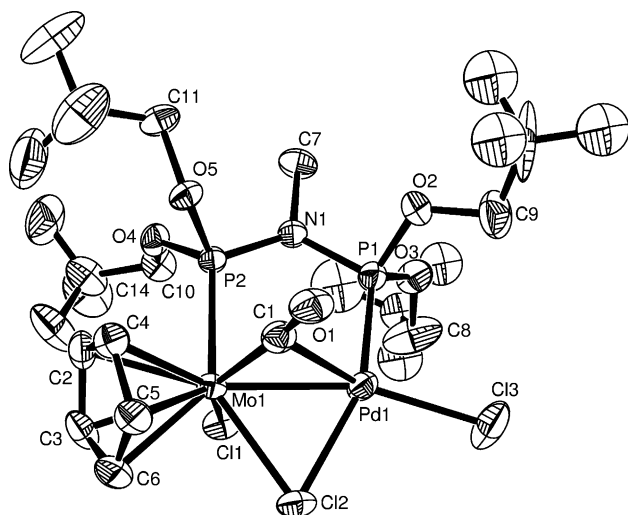


Fig. 6. The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{ClMo}(\mu_2\text{-CO})(\mu_2\text{-Cl})(\mu\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)\text{PdCl}]$ (**6a**).

Table 4
Selected bond distances (Å) and bond angles (°) in **3a**

Pd(1)–P(3)	2.246(3)	P(3)–Pd(1)–P(2)	179.3(1)
Pd(1)–P(2)	2.248(3)	P(3)–Pd(1)–Cl(1)	90.7(1)
Pd(1)–Cl(1)	2.440(3)	P(2)–Pd(1)–Cl(1)	89.9(1)
Pd(1)–Mo(1)	2.860(1)	P(3)–Pd(1)–Mo(1)	89.5(1)
Mo(1)–C(1)	1.95(1)	P(2)–Pd(1)–Mo(1)	90.0(1)
Mo(1)–P(4)	2.350(3)	Cl(1)–Pd(1)–Mo(1)	163.6(1)
Mo(1)–P(1)	2.354(3)	C(1)–Mo(1)–P(4)	75.9(3)
P(1)–N(1)	1.70(1)	C(1)–Mo(1)–P(1)	76.3(3)
P(2)–N(1)	1.65(1)	P(4)–Mo(1)–P(1)	118.7(1)
P(3)–N(2)	1.65(1)	C(1)–Mo(1)–Pd(1)	136.6(3)
P(4)–N(2)	1.67(1)	P(4)–Mo(1)–Pd(1)	81.82(7)
O(1)–C(1)	1.16(1)	P(1)–Mo(1)–Pd(1)	82.8(1)
		P(3)–N(2)–P(4)	114.4(5)
		P(2)–N(1)–P(1)	113.1(5)
		O(1)–C(1)–Mo(1)	178.4(10)

Table 5
Selected bond distances (Å) and bond angles (°) in **4b**

Mo(1)–P(1)	2.388(1)	C(1)–Mo(1)–P(1)	81.7(1)
Mo(1)–P(2)	2.420(1)	C(1)–Mo(1)–P(2)	103.2(1)
Mo(1)–C(1)	1.955(4)	P(1)–Mo(1)–P(2)	63.4(3)
Mo(1)–Cl(1)	2.518(1)	C(1)–Mo(1)–Cl(1)	83.5(1)
P(1)–N(1)	1.682(3)	P(1)–Mo(1)–Cl(1)	135.7(1)
P(2)–N(1)	1.679(3)	P(2)–Mo(1)–Cl(1)	80.0(1)
		Mo(1)–P(2)–P(1)	57.7(1)
		P(2)–N(1)–P(1)	97.5(1)
		O(1)–C(1)–Mo(1)	175.2(3)

Å] falls within the range [2.93–2.69 Å] observed for other dinuclear molybdenum–palladium complexes (Table 8). The mean Mo–P [2.352 Å] and Pd–P distances [2.245 Å] are shorter than those for the corresponding $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ complexes. This trend is in accord with

Table 6
Selected bond distances (Å) and bond angles (°) in **5b** (molecule 1)

Pd(1)–P(1)	2.211(5)	P(1)–Pd(1)–Cl(1)	94.4(2)
Pd(1)–Cl(1)	2.402(4)	P(1)–Pd(1)–Pd(2)	97.4(1)
Pd(1)–C(1)	2.54(2)	Cl(1)–Pd(1)–Pd(2)	168.2(1)
Pd(1)–Pd(2)	2.537(2)	P(1)–Pd(1)–Mo(1)	159.6(1)
Pd(1)–C(2)	2.58(1)	Cl(1)–Pd(1)–Mo(1)	105.9(1)
Pd(1)–Mo(1)	2.774(3)	Pd(2)–Pd(1)–Mo(1)	62.4(1)
Pd(2)–P(3)	2.245(3)	P(3)–Pd(2)–P(2)	105.8(1)
Pd(2)–P(2)	2.250(4)	P(3)–Pd(2)–Pd(1)	164.1(1)
Pd(2)–C(1)	2.46(2)	P(2)–Pd(2)–Pd(1)	90.1(1)
Pd(2)–C(2)	2.48(1)	P(3)–Pd(2)–Mo(1)	101.1(1)
Pd(2)–Mo(1)	2.758(2)	P(2)–Pd(2)–Mo(1)	152.7(1)
Mo(1)–P(4)	2.401(4)	Pd(1)–Pd(2)–Mo(1)	63.0(1)
Mo(1)–C(2)	1.98(2)	P(4)–Mo(1)–Pd(2)	81.2(1)
Mo(1)–C(1)	2.00(2)	P(4)–Mo(1)–Pd(1)	135.8(1)
P(4)–N(2)	1.68(1)	Pd(2)–Mo(1)–Pd(1)	54.6(1)
P(2)–N(1)	1.66(1)	P(3)–N(2)–P(4)	115.1(6)
P(3)–N(2)	1.67(1)	P(2)–N(1)–P(1)	117.0(8)
P(1)–N(1)	1.67(1)		

Table 7
Selected bond distances (Å) and bond angles (°) in **6a** (molecule 1)

Mo(1)–C(1)	1.99(1)	Cl(3)–Pd(1)–Cl(2)	104.1(2)
Mo(1)–P(2)	2.437(3)	P(1)–Pd(1)–Cl(3)	97.1(1)
Mo(1)–Cl(2)	2.479(3)	P(1)–Pd(1)–Cl(2)	156.4(1)
Mo(1)–Cl(1)	2.494(3)	P(1)–Pd(1)–Mo(1)	99.3(1)
Mo(1)–Pd(1)	2.629(2)	Cl(3)–Pd(1)–Mo(1)	162.9(1)
Pd(1)–P(1)	2.150(3)	Cl(2)–Pd(1)–Mo(1)	58.9(1)
Pd(1)–Cl(3)	2.352(4)	C(1)–Mo(1)–P(2)	85.1(4)
Pd(1)–Cl(2)	2.395(3)	C(1)–Mo(1)–Cl(2)	85.1(4)
Pd(1)–C(1)	2.45(1)	P(2)–Mo(1)–Cl(2)	141.9(1)
P(2)–N(1)	1.66(1)	C(1)–Mo(1)–Cl(1)	140.1(4)
P(1)–N(1)	1.67(1)	P(2)–Mo(1)–Cl(1)	82.6(1)
O(1)–C(1)	1.14(1)	Cl(2)–Mo(1)–Cl(1)	81.7(1)
		C(1)–Mo(1)–Pd(1)	62.1(4)
		P(2)–Mo(1)–Pd(1)	87.2(1)
		Cl(2)–Mo(1)–Pd(1)	55.8(1)
		Cl(1)–Mo(1)–Pd(1)	79.5(1)
		Pd(1)–Cl(2)–Mo(1)	65.2(1)
		P(2)–N(1)–P(1)	119.1(6)

the strong π -acceptor nature of the diphosphazane ligand. The mean Pd–P distance and the P–N–P angles are comparable to those in $[\text{Pd}_2\text{Cl}_2(\mu\text{-PhN}\{\text{P}(\text{OPh})_2\}_2)_2]$ [8].

The geometry around molybdenum in the monometallic chelate complex **4b** is that of a four-legged piano stool with *cisoidal* orientation of Cl and CO as reflected in the angles Cl–Mo–C(1) [83.5(1)°] and P(1)–Mo–P(2) [63.4(3)°]. The two phosphorus atoms are coordinated at different distances; the longer Mo–P(2) [2.420(1) Å] bond pertains to the phosphorus atom situated closer to the chloride ligand while the shorter [Mo–P(1) = 2.388(1) Å] distance corresponds to the phosphorus further from the chloride ligand. Both the distances are considerably shorter than those in the analogous dppe complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{dppe})\text{Cl}]$ [Mo–P = 2.496(4) Å, 2.439(5) Å] [36]. This trend again reflects

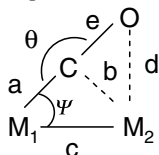
Table 8
The Mo–Pd bond distances in dinuclear Mo–Pd and trinuclear Mo–Pd₂ complexes

Complex	Mo–Pd (Å)	Reference
[(<i>t</i> -BuNC)(CO) ₃ Mo(μ-dppm) ₂ PdI]PF ₆	2.870(2)	[29]
[(<i>t</i> -BuNC)(CO)ClMo(μ-CO)(μ-dppm) ₂ PdCl]	2.826(2)	[29]
[(CN)(CO) ₃ Mo(μ-dppm) ₂ PdCN]	2.926(2)	[29]
[PdMo(μ-CO)(CO)(η ⁵ -C ₅ H ₅)(dppm) ₂][PF ₆]	2.799(1)	[24]
[PdMo(μ-Ph ₂ Ppy) ₂ (μ-CO)(CO) ₂ Cl ₂]	2.817(1)	[27]
[PdMo(μ-PCy ₂) ₂ {PH(Cy) ₂ } ₂ (η ⁵ -C ₅ H ₅)(CO) ₂]	2.916(2)	[30]
[PdMo(μ-PCy ₂) ₂ (PPh ₃)(CO) ₄]	2.760(1)	[31]
[PdMo(μ-PPh ₂) ₂ (CO) ₄ PPh ₃]	2.748(1)	[32]
[PdI{μ-C(<i>p</i> -tolyl)-dmba}{μ-CO}Mo(Cp)(<i>t</i> -BuNC) ₂]	2.692(2)	[33]
[C(<i>p</i> -tolyl)-dmba = Me ₂ NCH ₂ C ₆ H ₄ –C ₆ H ₄ –Me- <i>p</i>]		
[(η ⁵ -C ₅ H ₅)(CO)Mo(μ-MeN{P(OCH ₂ CF ₃) ₂) ₂ PdCl], 3a	2.86(1)	This work
[(η ⁵ -C ₅ H ₅)ClMo(μ ₂ -CO)(μ ₂ -Cl)(μ-MeN{P(OCH ₂ CF ₃) ₂) ₂ PdCl], 6a	2.63(1)	This work
[Pd ₂ Mo(η ⁵ -C ₅ H ₅)(Cl)(μ ₃ -CO) ₂ (μ-dppm) ₂]	2.779(1)	[26]
	2.783(1)	
[Pd ₂ Mo(η ⁵ -C ₅ H ₅) ₂ (CO) ₃ (P ^{<i>i</i>} Pr ₃) ₂]	2.803(1)	[34]
	2.781(1)	
[{PdNMe ₂ CH ₂ C ₆ H ₄ }] ₂ μ{Mo(CO) ₃ (η ⁵ -C ₅ H ₅) ₂ μ-Cl}	2.832(1)	[35]
	2.788(1)	
[(η ⁵ -C ₅ H ₅)Mo(μ ₃ -CO) ₂ (μ-MeN{P(OPh) ₂ } ₂) ₂ Pd ₂ Cl] · CH ₂ Cl ₂ , 5b	2.774(3)	This work
	2.758(2)	

Table 9
Bond parameters related to semibridging carbonyls in **5b** and **6a**^a

Complex	α ^b	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Å)	<i>e</i> (Å)	θ (°)	ψ (°)
5b								
Pd(2), C(1)	0.23	2.00	2.46(2)	2.758(2)	3.18(1)	1.14(2)	164.0(1)	59.9(4)
Pd(2), C(2)	0.25	1.98(2)	2.479(14)	2.758(2)	3.19(1)	1.18(2)	167.1(1)	60.4(4)
Pd(1), C(1)	0.27	2.00	2.54(2)	2.774(3)	3.19(1)	1.14(2)	164.0(1)	61.8(5)
Pd(1), C(2)	0.30	1.98(2)	2.579(14)	2.774(3)	3.22(1)	1.18(2)	167.1(1)	63.1(4)
6a	0.23	1.993(14)	2.445(13)	2.629(2)	3.12(1)	1.14(1)	171.8(1)	62.1(4)

^a The parameters *a*, *b*, *c*, *d*, *e*, θ and ψ are defined as shown below [43]:



^b α is defined as (b – a)/a [40].

the strong π-acceptor capability of the diphosphazane ligand. The P(1)–Mo–P(2) [63.4(1)°] angle is smaller than the corresponding P(1)–Mo(1)–P(2) angle [75.3°] found in the dppe complex, but is comparable to that observed for the Diphosphazane complex, [Mo(CO)₄(PhN{P(OPh)₂}₂)] [P(1)–Mo–P(2) = 64.8(1)°] [7]. The P(1)–N(1)–P(2) angle [97.5(1)°] is close to that observed for the diphosphazane chelate complexes, [Mo(CO)₄(PhN{P(OPh)₂}₂)] [7] and [Wl₂(CO)₃(PhN{P(OPh)₂}₂)] [37].

The solid state structure of the trimetallic complex **5b** reveals the presence of two independent molecules in the asymmetric part of the unit cell. The two molecules do not differ in their bond lengths and bond angles but differ in the orientation of the phenyl groups. The molecules consist of a triangulo Pd(1)–Pd(2)–Mo(1) unit, of which the edges Pd(1)–Pd(2) and Pd(2)–Mo(1) are spanned by the diphosphazane ligand. The Pd(1)–

Pd(2), Pd(1)–Mo(1), Pd(2)–Mo(1) distances are slightly shorter than those in the related trinuclear clusters (Table 8). The two carbonyl ligands are semi-bridging with respect to the two Pd centers and are slightly closer to Pd(2) than to Pd(1). One CO is located above and the other below the Pd₂Mo plane [distances from this plane to C(1) and C(2) are 1.670(6) and 1.676(6) Å, respectively] These two carbonyl ligands are slightly bent [Mo(1)–C(1)–O(1) = 164(1)°, Mo(1)–C(2)–O(2) = 167(1)°]. The P(4)–Mo(1)–Pd(2) angle [81.2(1)°] is less than the P(3)–Pd(2)–Mo(1), P(2)–Pd(2)–Pd(1) and P(1)–Pd(1)–Pd(2) angles presumably because of the steric interaction between the C₅H₅ ligand and the phenyl groups at P(4). The Pd(1)–Cl distance [2.402(4) Å] is comparable to that found in [Pd₂Cl₂(PhN{P(OPh)₂}₂)₂]; however, the Pd–Pd distance is shorter (by 0.082 Å) [8].

The solid state structure of **6a** consists of two independent molecules in the asymmetric part of the unit cell. The bond lengths and bond angles in the two molecules do not differ significantly. The two molecules differ in the orientation of trifluoroethoxy groups. The coordination geometry around the Mo atom (ignoring the M–M bond) is that of a four-legged piano stool with the two chlorides adopting a *cisoid* orientation. The formal oxidation state of Mo is +2.5 and that of Pd is +1.5 and hence there is a dative bond between palladium and molybdenum. An interesting feature of the complex is the presence of a semibridging CO as well as a bridging chloride. If the bridging chloride is considered as a one electron donor, the total number of valence electrons for this compound would be 30 which implies a formal double bond between Mo and Pd. This is reflected in the Mo–Pd distance [2.63(1) Å] which is 0.23 Å shorter than that for **3a** [2.86(1) Å] having a Mo–Pd single bond and also 0.20–0.29 Å shorter than that found in several Mo–Pd heteronuclear complexes containing dppm and other ligands (Table 8). Casey et al. [38] have concluded that there is a double bond between two Re atoms in [Cp*(CO)₂Re=Re(CO)₂Cp*] based on the Re–Re bond distance and the linear nature of the semi-bridging carbonyl ligand. The Mo–P [2.437(3) Å] and Pd–P [2.150(3) Å] distances in **6a** are shorter than the Mo–P and Pd–P distances for the dppm complexes. The P(1)–N(1)–P(2), P(1)–Pd(1)–Mo(1) and P(2)–Mo(1)–Pd(1) angles are wider than the corresponding angles for **3a**. The Cl(3)–Pd(1)–Mo(1) angle [162.9(1) Å] deviates from linearity probably because of the tilt of one of the CF₃ groups towards the chloride ligand.

The description of bonding of semi-bridging carbonyls to transition metals has been the subject of several investigations [39–44]. Following the approach of Crabtree and Lavin [43], the various parameters '*a*, *b*, *c*, *d*, *e*, *θ* and *Ψ*' for the semi-bridging carbonyls in **5b** and **6a** are listed in Table 9. The value of the parameter *α* as defined by Curtis and coworkers [40] is also included in Table 9. These values for both **5b** and **6a** fall within the range found for type II linear semi-bridging carbonyls. Theoretical studies have shown that linear semi-bridging carbonyls would be associated with strong M–M bonding interactions [45]. Both the carbonyls in **5b** have shorter distances with Pd(2) than with Pd(1). Consequently, the Pd(2)–Mo distance [2.758(2) Å] is shorter than the Pd(1)–Mo distance [2.774(3) Å], which in turn implies that the Pd(2)–Mo bond is slightly stronger than Pd(1)–Mo bond.

4. Conclusions

Heterometallic complexes of palladium with other transition metals bearing bidentate phosphorus ligands such as Ph₂PXPPH₂ [X = CH₂ or NH] (L–L) have been

prepared generally by the reactions of the (chloro)palladium(I) dimer, [PdCl(L–L)]₂ with metal carbonylate anions, [M(CO)_{*n*}][–] or [CpM(CO)_{*n*}][–] [6,26,46]. The present study demonstrates that a direct thermal reaction between metal–metal bonded dipalladium and dimolybdenum complexes leads to Mo–Pd dinuclear, MoPd₂ trinuclear and mononuclear molybdenum chelate complexes [47]. While trinuclear complexes of type **5** are not unprecedented and the formation of dinuclear complexes of type **3** is not unexpected, dinuclear complexes of type **6** with chloro and carbonyl bridges are unusual. Given the range of diphosphazane ligands in which the substituents on both phosphorus and nitrogen can be varied readily [3a], it would be interesting to investigate systematically the “metathesis” reactions of metal–metal bonded systems to enlarge the scope of the synthetic strategy developed in the present study and also to unravel the mechanism(s) involved in the formation of trinuclear and unusual dinuclear complexes from these reactions.

5. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 244244–244248 for compounds **1a**, **3a**, **4b**, **5b** and **6a**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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References

- [1] P. Braunstein, L.A. Oro, P.R. Raithby, Metal Clusters in Chemistry, vol. 2, Wiley-VCH, Weinheim, 2000.
- [2] E.W. Abel, F.G.A. Stone, G. Wilkinson, Comprehensive Organometallic Chemistry II, vol. 10, Pergamon, Oxford, 1995.
- [3] (a) M.S. Balakrishna, V.S. Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1;
(b) M. Ganesan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 570 (1998) 247;
(c) K. Raghuraman, S.S. Krishnamurthy, M. Nethaji, J. Chem. Soc., Dalton Trans. (2002) 4289;
(d) S.K. Mandal, S.S. Krishnamurthy, G.A.N. Gowda, M. Nethaji, Dalton Trans. (2003) 1016;

- (e) K. Raghuraman, S.S. Krishnamurthy, M. Nethaji, *J. Organomet. Chem.* 669 (2003) 79;
- (f) S.K. Mandal, S.S. Krishnamurthy, M. Nethaji, *J. Organomet. Chem.* 676 (2003) 22;
- (g) T.S. Venkatakrishnan, M. Nethaji, S.S. Krishnamurthy, *Current Sci.* 85 (2003) 969;
- (h) S.K. Mandal, G.A.N. Gowda, S.S. Krishnamurthy, T. Stey, D. Stalke, *J. Organomet. Chem.* (in press).
- [4] Part of this work was presented at the XIV International Conference on Phosphorus Chemistry, Cincinnati, Ohio, USA, July 12–17, 1998. M. Ganesan, S.S. Krishnamurthy, M. Nethaji, K. Raghuraman, *Phosphorus Sulfur Silicon* 147 (1999) 355.
- [5] (a) J.T. Mague, *Organometallics* 10 (1991) 513;
- (b) J.T. Mague, Z. Lin, *Organometallics* 11 (1992) 4139.
- [6] (a) I. Bachert, P. Braunstein, R. Hasselbring, *New J. Chem.* 20 (1996) 993;
- (b) I. Bachert, P. Braunstein, M.K. McCart, F. Fabrizi de Biani, F. Laschi, P. Zanello, G. Kickelbick, U. Schubert, *J. Organomet. Chem.* 573 (1999) 47;
- (c) I. Bachert, I. Bartussek, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, *J. Organomet. Chem.* 588 (1999) 144.
- [7] M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, U. Siriwardane, N.S. Hosmane, *J. Organomet. Chem.* 390 (1990) 203.
- [8] M.S. Balakrishna, S.S. Krishnamurthy, R. Murugavel, M. Nethaji, I.I. Mathews, *J. Chem. Soc., Dalton Trans.* (1993) 477.
- [9] M.D. Curtis, M.S. Hay, M. Gunchoi, R.J. Angelici, *Inorg. Synth.* 28 (1990) 150.
- [10] D. Drew, J.R. Doyle, *Inorg. Synth.* 28 (1990) 346.
- [11] G.M. Sheldrick, *SHELXS-86* and *SHELXL-93*, Universitat Göttingen, 1986 and 1993.
- [12] Two other products are formed in this reaction as shown by the ^{31}P NMR spectrum of the reaction mixture; the singlet observed at 76.5 ppm is assigned to the chelate complex, $[\text{PdCl}_2(\kappa^2\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}_2)]$ (based on the ^{31}P chemical shift for the analogous complex $[\text{PdCl}_2(\kappa^2\text{-MeN}\{\text{P}(\text{OC}_6\text{H}_5)_2\}_2)]$) [8] and the multiplets at 98.4 and 0.8 ppm are assigned to the P-coordinated diphosphazane-monoxide complex, $[\text{PdCl}_2(\kappa^1\text{-MeN}\{\text{P}(\text{OCH}_2\text{CF}_3)_2\}\{\text{P}(\text{O})(\text{OCH}_2\text{CF}_3)_2\}_2)]$.
- [13] L.S. Benner, A.L. Balch, *J. Am. Chem. Soc.* 100 (1978) 6099.
- [14] C. Amatore, E. Carre, A. Jutand, M.A. M'Barki, *Organometallics* 14 (1995) 1818.
- [15] V.V. Grushin, H. Alper, *Organometallics* 12 (1993) 1890.
- [16] C. Amatore, A. Jutand, M.J. Medeiros, *New J. Chem.* 20 (1996) 1143.
- [17] M.R. Mason, J.G. Verkade, *Organometallics* 11 (1992) 2212.
- [18] P.A. McLaughlin, J.G. Verkade, *Organometallics* 17 (1998) 5937.
- [19] Z. Csakai, R. Skoda-Foeldes, L. Kollar, *Inorg. Chim. Acta* 286 (1999) 93.
- [20] R. Uson, J. Fornies, R. Navarro, M. Tomas, C. Fortuno, J.I. Cebollada, *Polyhedron* 8 (1989) 1045.
- [21] R.B. King, J. Gimeno, *Inorg. Chem.* 17 (1978) 2396.
- [22] T.K. Prakasha, Transition metal organometallic complexes and related derivatives of bis(diphenylphosphino)isopropylamine and bicyclic 1,3,2 λ^3 ,4 λ^3 -diazadiphosphetidines, Ph.D. Thesis, Indian Institute of Science, Bangalore, 1990, pp. 79–80.
- [23] R.J. Haines, R.S. Nyholm, M.H.B. Stiddard, *J. Chem. Soc. A* (1968) 43.
- [24] P. Braunstein, B. Oswald, A. DeCian, J. Fischer, *J. Chem. Soc., Dalton Trans.* (1991) 2685.
- [25] K. Starker, M.D. Curtis, *Inorg. Chem.* 24 (1985) 3006.
- [26] P. Braunstein, M. Ries, C. de Meric de Bellefon, Y. Dusausoy, J.-P. Mangeot, *J. Organomet. Chem.* 355 (1988) 533.
- [27] Z.-Z. Zhang, H.-K. Wang, H.-G. Wang, R.-J. Wang, *J. Organomet. Chem.* 314 (1986) 357.
- [28] W. Klaui, H. Hamers, M. Pfeffer, A. de Cian, J. Fischer, *J. Organomet. Chem.* 394 (1990) 213.
- [29] A.L. Balch, B.C. Noll, M.M. Olmstead, D.V. Toronto, *Inorg. Chem.* 32 (1993) 3613.
- [30] P. Braunstein, E. de Jesus, A. Tiripicchio, M.T. Camellini, *J. Organomet. Chem.* 368 (1989) C5.
- [31] S.J. Loeb, H.A. Taylor, L. Gelmini, D.W. Stephan, *Inorg. Chem.* 25 (1986) 1977.
- [32] Z. He, N. Lugan, D. Neibecker, R. Mathieu, J.-J. Bonnet, *J. Organomet. Chem.* 426 (1992) 247.
- [33] A. Macchioni, P.S. Pregosin, P.F. Engel, S. Mecking, M. Pfeffer, J.-C. Daran, J. Vaissermann, *Organometallics* 14 (1995) 1637.
- [34] H. Werner, P. Thometzek, C. Krueger, H.-J. Kraus, *Chem. Ber.* 119 (1986) 2777.
- [35] M. Pfeffer, J. Fischer, A. Mitschler, L. Ricard, *J. Am. Chem. Soc.* 102 (1980) 6338.
- [36] M.A. Bush, A.D.U. Hardy, L. Manojlovic-Muir, G.A. Sim, *J. Chem. Soc. A* (1971) 1003.
- [37] M.S. Balakrishna, S.S. Krishnamurthy, H. Manohar, *Organometallics* 10 (1991) 2522.
- [38] C.P. Casey, H. Sakaba, P.N. Hazin, D.R. Powell, *J. Am. Chem. Soc.* 113 (1991) 8165.
- [39] F.A. Cotton, *Prog. Inorg. Chem.* 21 (1976) 1.
- [40] R.J. Klingler, W.M. Butler, M.D. Curtis, *J. Am. Chem. Soc.* 100 (1978) 5034.
- [41] R. Colton, M.J. McCormick, *Coord. Chem. Rev.* 31 (1980) 1.
- [42] E.D. Jemmis, A.R. Pinhas, R.J. Hoffmann, *J. Am. Chem. Soc.* 102 (1980) 2576.
- [43] R.H. Crabtree, M. Lavin, *Inorg. Chem.* 25 (1986) 805.
- [44] M. Benard, A. Dedieu, S. Nakamura, *Nouv. J. Chim.* 8 (1984) 149.
- [45] C.Q. Simpson, M.B. Hall, *J. Am. Chem. Soc.* 114 (1992) 1641.
- [46] (a) P. Braunstein, C. de Meric de Bellefon, M. Ries, J. Fischer, S.-E. Bouaoud, D. Grandjean, *Inorg. Chem.* 27 (1988) 1327;
- (b) P. Braunstein, C. de Meric de Bellefon, M. Ries, *Inorg. Chem.* 27 (1988) 1338;
- (c) P. Braunstein, C. de Meric de Bellefon, M. Ries, J. Fischer, *Organometallics* 7 (1988) 332.
- [47] Chelate complexes of the type **4** have been obtained by the reactions of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}]$ with diphosphines [25].