



The preparation of multimetallic complexes using sterically bulky N-centred tripodal dialkyl phosphino ligands

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ABSTRACT

Sterically bulky monodentate and bidentate phosphines have been widely used as ligands for metal complexation and catalyst formation. Bulky tridentate phosphine ligands are however much rarer and have not been widely investigated even though they may be considered attractive ligands for coordination chemistry studies and catalysis. Here we report the synthesis of two new N-centred tripodal phosphine ligands bearing bulky cyclohexyl and *tert*-butyl groups. The coordination chemistry of the cyclohexyl triphosphine ligand $\text{N}(\text{CH}_2\text{PCy}_2)_3$ (**4**) was investigated and found to react with Mo and W hexacarbonyls preferentially forming bidentate metal tetracarbonyl complexes $[\text{Mo}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3-\kappa^2\text{P}\}]$ (**6**) and $[\text{W}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3-\kappa^2\text{P}\}]$ (**7**) over the expected facial capping tridentate complexes. The steric bulk of the cyclohexyl groups on the phosphorus atoms is sufficient to prevent the third arm of the ligand from coordinating and adopting the required geometry for facial coordination. This 'steric control' at the metal centre results in the third arm remaining freely available for further metal coordination. The coordination chemistry of this free phosphine arm on complexes **6** and **7** was investigated further and used to prepare a series of gold, platinum and silver multimetallic complexes. The X-ray crystal structures of the resulting mixed bi and trimetallic complexes $[\text{W}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3-\kappa^2\text{P}\}\text{AuCl}]$ (**8**), $[[\text{Mo}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3-\kappa^2\text{P}\}]_2(\mu\text{-PtCl}_2)]$ (**9**) and $[[\text{W}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3-\kappa^2\text{P}\}]_2(\mu\text{-Ag})\text{ClO}_4]$ (**11**) are reported.

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1. Introduction

Triphosphine ligands have generated considerable interest for the preparation of transition metal complexes and catalysts over the past three decades [1–3]. The tripodal phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane ($\text{CH}_3(\text{CH}_2\text{PPh}_2)_3$, triphos, **1**) is one of the most widely studied triphosphine ligands and has been shown to form an extensive range of metal complexes [4–12] and a number of active catalytic species [13–18]. New triphos-type ligands continue to attract interest for the preparation of coordination complexes [19–24], however, their synthesis is not always trivial. Triphos ligands are commonly prepared via the nucleophilic substitution of a suitable alkyltrihalide backbone with a dialkyl/diaryl phosphide generated from the corresponding secondary phosphine. The necessary phosphide reagents can be challenging to prepare and the complete substitution of all three halide leaving groups can be difficult to achieve in high yields. Although a range of aryl triphos derivatives have been prepared in this way [20], relatively few alkyl triphos derivatives have appeared in the literature to date even though they may be considered attractive ligands for coordination chemistry studies and catalytic applications. The lack of alkyl triphos derivatives reported

in the literature may be associated with difficulties in their synthesis *i.e.* inefficient generation of alkylphosphides from the air sensitive secondary phosphines and incomplete substitution of halide leaving groups on the alkyl backbone which may result in poor yields. A general, high yielding and straightforward synthetic route to a broad range of triphos-type ligands, especially those containing dialkylphosphino groups, would therefore be of interest.

The previously reported amino bridged triphosphine ligand tris(diphenylphosphinomethyl)amine ($\text{N}(\text{CH}_2\text{PPh}_2)_3$, N-triphos, **2**) is structurally analogous to the parent triphos ligand except for a nitrogen atom at the bridgehead instead of a C-CH₃ group. Considering the similarity of these two ligands and widespread use of triphos for metal complexation and catalytic studies, it is surprising that there have been very few reports on the coordination chemistry or catalysis using this N-triphos ligand [25–28]. In comparison, the more flexible tris(diphenylphosphinoethyl)amine ligand (**3**), with an ethyl spacer between the bridgehead nitrogen and P atoms, has received much more attention [3,29]. The greater length and flexibility of the ethyl spacers of this ligand can result in the central bridgehead N-atom competing with the phosphorus atoms for metal coordination sites which can result in a mixture of isomers. In contrast the bridgehead nitrogen atom of N-triphos may be believed to behave in an 'innocent' fashion, with regards to competition with the surrounding P atoms for metal coordination, since the formation of a four-membered chelate ring would be

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unfavourable. Thus the coordination chemistry of N-triphos ligands may be considered to behave in an analogous manner to that of triphos. Additionally, compared to the synthetic routes used to prepare standard triphos-type ligands, N-triphos-type ligands are relatively straightforward to prepare and therefore present greater opportunities for developing new triphosphine ligands with varied diaryl or dialkyl phosphino groups. Here, we report the synthesis of two new N-triphos ligands bearing bulky dicyclohexyl (**4**) and di-*tert*-butyl (**5**) phosphino groups, prepared by a straightforward and general synthetic route, and investigate the coordination chemistry of the cyclohexyl ligand N(CH₂PCy₂)₃ (**4**).

2. Experimental

2.1. General considerations

All preparations were carried out using standard Schlenk line techniques under an inert atmosphere of N₂ unless otherwise stated. Solvents were dried over standard drying agents and freshly distilled under nitrogen before use. All starting materials were of reagent grade, purchased from either Aldrich Chemical Company or Strem Chemicals. Aryl and alkyl (hydroxymethyl)phosphonium chloride salts were prepared according to literature methods [30]. Chromatographic separations were carried out on Kieselgel 60 SiO₂. ¹H, ¹³C and ³¹P{¹H} NMR spectra were recorded on Bruker Av-400, DRX-400, Av-500 spectrometers. Chemical shifts are reported in ppm using the residual proton impurities in the solvents. Pseudo-triplets which occur as a result of identical *J*-value coupling to two chemically inequivalent nuclei are assigned as dd and are recognised by the inclusion of only one *J*-value. Positive-ion FAB and electron ionisation mass spectra were recorded on a Micro-mass Autospec Q spectrometer using a 3-nitrobenzyl alcohol matrix. Electron ionisation was carried out at 70 eV. Infrared spectra were recorded on a Perkin–Elmer 983G spectrophotometer equipped with a Perkin–Elmer 3700 data station and recorded as a solution in dichloromethane. Elemental analyses were carried out by Mr. Stephen Boyer of the Department of Health and Human Sciences, London Metropolitan University. X-ray diffraction analysis was carried out by Dr. Andrew White of the Department of Chemistry at Imperial College London.

2.2. Synthesis of N,N,N-tris(diphenylphosphinomethyl)amine (**2**)

To a Schlenk flask was added diphenyl(hydroxymethyl)phosphonium chloride (7.75 g, 27.4 mmol), ammonium chloride (0.49 g, 9.14 mmol), degassed methanol (100 ml) and triethylamine (7.4 ml, 55.0 mmol). The mixture heated under reflux for 2 h, during which a white precipitate formed. The precipitate was filtered in air and washed with methanol (3 × 30 ml). (4.5 g, 81%). Characterisation data was consistent with that reported in the literature [25,26]. ¹H NMR (CDCl₃, 400 MHz): δ 7.40–7.22 (m, 30 H, PPh₂), 3.82 (d, 6 H, ²J_{PH} = 3.29 Hz, CH₂P). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ –28.9 (s).

2.3. Synthesis of N,N,N-tris(dicyclohexylphosphinomethyl)amine (**4**)

To a Schlenk flask was added dicyclohexyl(hydroxymethyl)phosphonium chloride (588 mg, 2.0 mmol), ammonium chloride (35 mg, 0.67 mmol), degassed methanol (10 ml) and triethylamine (0.45 ml, 10 mmol). The mixture heated under reflux for 2 h. A white precipitate was noticed to form almost immediately on heating to reflux. Methanol was removed via cannula filtration and the white solid rinsed with methanol (2 × 10 ml) and dried *in vacuo* and isolated as a white powder that was stored under a nitrogen atmosphere. (360 mg, 84%). Anal. Calc. for

C₃₉H₇₂NP₃: C, 72.30; H, 11.20; N, 2.16. Found: C, 72.39; H, 10.97; N, 2.08%. IR (ν/cm⁻¹): ¹H NMR (CDCl₃, 400 MHz): δ 2.89 (s, br, 6H, CH₂P), 1.83–1.25 (m, 66H, cyclohexyl). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ –17.0 (s). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 54.8 (s, br, CH₂P), 32.7 (d, ¹J_{PC} = 12.4 Hz P-CH₂cyclohexyl), 30.0 (d, ²J_{PC} = 11.8 Hz CH₂cyclohexyl), 29.8 (d, ²J_{PC} = 11.5 Hz CH₂cyclohexyl), 27.5 (d, ³J_{PC} = 7.8 Hz CH₂cyclohexyl), 27.3 (d, ³J_{PC} = 8.8 Hz CH₂cyclohexyl), 26.6 (s, CH₂cyclohexyl). TOF-MS ES: *m/z* (%): 734 (5), 718 (48), 696 (50), 680 (95), 482 (100).

2.4. Synthesis of N,N,N-tris(ditert-butylphosphinomethyl)amine (**5**)

To a Schlenk flask was added di-*tert*-butyl(hydroxymethyl)phosphonium chloride (243 mg, 1.0 mmol), ammonium chloride (18 mg, 0.33 mmol), degassed methanol (5 ml) and triethylamine (0.24 ml, 5 mmol). The mixture was heated under reflux overnight. The volume was reduced to approximately one third by removal of methanol *in vacuo*, which resulted in the precipitation of a white solid. Recrystallisation of this mixture by heating and slow cooling to room temperature resulted in the formation of colourless crystals suitable for X-ray diffraction studies. Methanol was removed via cannula filtration and the crystals dried *in vacuo* and stored under a nitrogen atmosphere. (84 mg, 52%). Anal. Calc. for C₂₇H₆₀NP₃: C, 65.95; H, 12.30; N, 2.85. Found: C, 65.81 H, 12.53; N, 2.93%. IR (ν/cm⁻¹): 3054, 2951, 1472, 1421, 1366, 1062, 896, 811. ¹H NMR (CDCl₃, 400 MHz): δ 2.90 (s, br, 6H, CH₂P), 1.18 (d, 54H, ²J_{PH} = 12.4 Hz, *t*Bu). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ –12.5 (s). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 56.5 (d, ¹J_{PC} = 10.2 Hz, CH₂P), 31.7 (d, ¹J_{PC} = 21.2 Hz, P-C(CH₃)₃), 30.0 (d, ²J_{PC} = 14.0 Hz, PC(CH₃)₃). TOF-MS ES: *m/z* (%): 581 (6), 565 (25), 549 (60), 533 (100).

2.5. Synthesis of [Mo(CO)₄{N(CH₂PCy₂)₃-κ²P}] (**6**)

To Schlenk flask was added N(CH₂PCy₂)₃ (360 mg, 0.56 mmol), Mo(CO)₆ (149 mg, 0.56 mmol) and DMF (5 ml). The reaction mixture heated to 100 °C for 2 h during which the evolution of CO gas was observed and colour change from colourless to light brown. After this time the reaction was allowed to cool to ambient temperature. White crystals suitable for X-ray diffraction formed on standing overnight. DMF was removed via cannula filtration and the crystals washed with diethyl ether (3 × 10 ml) and dried *in vacuo*. (320 mg, 67%). Anal. Calc. for C₄₃H₇₂MoNO₄P₃: C, 60.34; H, 8.48; N, 1.64. Found: C, 60.39; H, 8.50; N, 1.65%. IR (ν/cm⁻¹): 2930, 2008 (s), 1888 (br). ¹H NMR (CDCl₃, 400 MHz): δ 2.89 (s, br, 4H, CH₂P), 2.68 (s, br, 2H, CH₂P), 2.04–1.27 (m, 66H, cyclohexyl). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 22.8 (s, 2P, PCy₂-Mo), –16.7 (s, 1P, PCy₂). LSIMS: *m/z* (%): 856 (5) [M]⁺, 829 (5) [Mo(CO)₃{N(CH₂PCy₂)₃-κ²P}]⁺, 799 (5) [Mo(CO)₂{N(CH₂PCy₂)₃-κ²P}]⁺, 771 (10) [Mo(CO){N(CH₂PCy₂)₃-κ²P}]⁺, 211 (100).

2.6. Synthesis of [W(CO)₄{N(CH₂PCy₂)₃-κ²P}] (**7**)

This complex was prepared by an analogous method to that described for the Mo complex using N(CH₂PCy₂)₃ (340 mg, 0.53 mmol) and W(CO)₆ (185 mg, 0.53 mmol). (400 mg, 80%). Anal. Calc. for C₄₃H₇₂WNO₄P₃: C, 54.72; H, 7.69; N, 1.48. Found: C, 54.77; H, 7.78; N, 1.52%. IR (ν/cm⁻¹): 3056, 2931, 2854, 2004 (s), 1878 (br), 1448, 1421, 1274, 1266, 1258, 896. ¹H NMR (CDCl₃, 400 MHz): δ 2.97 (s, br, 4H, CH₂P), 2.67 (s, br, 2H, CH₂P), 2.06–1.26 (m, 66H, cyclohexyl). ³¹P{¹H} NMR (CDCl₃, 162 MHz): δ 3.2 (s, 2P, PCy₂-W) with W satellites (d, ¹J_{183W,P} = 217.3 Hz), –16.9 (s, 1P, PCy₂). LSIMS: *m/z* (%): 943 (52) [M]⁺, 915 (15) [W(CO)₃{N(CH₂PCy₂)₃-κ²P}]⁺, 887 (5) [W(CO)₂{N(CH₂PCy₂)₃-κ²P}]⁺, 860 (7) [W(CO){N(CH₂PCy₂)₃-κ²P}]⁺, 211 (100).

2.7. Synthesis of $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}AuCl]$ (**8**)

To a solution of **7** $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]$ (94 mg, 0.1 mmol) in dichloromethane (4 ml) was added $[AuCl(SMe)_2]$ (29.5 mg, 0.1 mmol) and the reaction mixture stirred overnight. Colourless crystals were obtained by diffusion of diethyl ether into this solution over a period of two days. The crystals were collected by filtration, rinsed with diethyl ether and dried *in vacuo*. (100 mg, 85%). Anal. Calc. for $C_{43}H_{72}AuClNO_4P_3W$: C, 43.91; H, 6.17; N, 1.19; Found: C, 43.90; H, 6.27; N, 1.13%. IR (ν/cm^{-1}): 2932, 2361, 2006 (s), 1879 (br), 1262. 1H NMR ($CDCl_3$, 400 MHz): δ 2.90 (s, br, 4H, CH_2P), 2.65 (s, br, 2H, CH_2P), 2.03–1.29 (m, 66H, cyclohexyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 13.8 (s, 1P), 6.8 (s, 2P, PCy_2-W) with W satellites (d, $^1J_{183W,P} = 219$ Hz). LSIMS: m/z (%): 1175 (10) $[M]^+$, 1063 (100) $[W(CO)\{N(CH_2PCy_2)_3-\kappa^2P\}AuCl]$.

2.8. Synthesis of $[Mo(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]_2(\mu-PtCl_2)$ (**9**)

To a solution of **6** $[Mo(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]$ (92 mg, 0.107 mmol) in dichloromethane (5 ml) was added $[PtCl_2(COD)]$ (20 mg, 0.054 mmol) and the reaction mixture stirred for one hour during which a white insoluble precipitate formed. The precipitate was collected by filtration, washed with diethyl ether and dried *in vacuo* (90 mg, 85%). The dichloromethane filtrate from this separation was collected and layered with diethyl ether. Crystals suitable for X-ray diffraction formed after a period of 4 days (10 mg, 10%). Anal. Calc. for $C_{86}H_{144}Cl_2N_2O_8P_6PtMo_2$: C, 52.23; H, 7.34; N, 1.42; Found: C, 52.26; H, 7.48; N, 1.32%. IR (ν/cm^{-1}) KBr Nujol mull: 2010, 1895, 1882, 1863, 1460, 1377, 1170, 1104, 852, 7222, 618, 592. $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 162 MHz): δ 29.1 (s, 4P, PCy_2-Mo), 16.3 (s, 2P, PCy_2-Pt). LSIMS: m/z (%): 1977 (10) $[M]^+$, 1750 (40) $[Mo\{N(CH_2PCy_2)_3-\kappa^2P\}]_2(\mu-PtCl_2)^+$, 1009 (100) $[Mo\{N(CH_2PCy_2)_3-\kappa^2P\}PtCl_2]^+$.

2.9. Synthesis of $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]_2(\mu-PtCl_2)$ (**10**)

To a solution of **7** $[Mo(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]$ (94 mg, 0.1 mmol) in dichloromethane (5 ml) was added $[PtCl_2(COD)]$ (18.5 mg, 0.05 mmol) and the reaction mixture stirred for 1 h during which time a white insoluble precipitate formed. This was filtered, washed with diethyl ether and dried *in vacuo* (97 mg, 90%). Anal. Calc. for $C_{86}H_{144}Cl_2N_2O_8P_6PtW_2$: C, 47.96; H, 6.74; N, 1.30; Found: C, 48.02; H, 6.65; N, 1.26%. IR (ν/cm^{-1}) KBr Nujol mull: 2007, 1889, 1871, 1860, 1460, 1377, 1104, 722, 605. LSIMS: m/z (%): 2153 (55) $[M]^+$, 2125 $[M]^+-CO$ (5), 746 (100).

2.10. Synthesis of $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]_2(\mu-Ag)ClO_4$ (**11**)

To a solution of **7** $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}]$ (94 mg, 0.1 mmol) in dichloromethane (5 ml) was added $AgClO_4$ (10.4 mg, 0.05 mmol) and the reaction mixture stirred overnight. Colourless crystals, suitable for X-ray diffraction, were obtained by diffusion of diethyl ether into this solution over a period of four days. The crystals were collected by filtration, rinsed with diethyl ether and dried *in vacuo*. (68 mg, 64%) Anal. Calc. for $C_{86}H_{144}AgClN_2O_8P_6W_2$: C, 49.31; H, 6.93; N, 1.34; Found: C, 49.22; H, 6.89; N, 1.29%. IR (ν/cm^{-1}): 3055, 2930, 2305, 2006 (s), 1880 (br), 1421, 1297, 1272, 1269, 896. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 13.8 (dd, $^1J_{109Ag,P} = 503$ Hz, $^1J_{107Ag,P} = 460$ Hz), 7.8 (s, 4P, PCy_2-W) with W satellites (d, $^1J_{183W,P} = 218$ Hz). LSIMS: m/z (%): 1996 (25) $[M]^+$, 1968 (5) $[M]^+-CO$, 1052 (60) $[W(CO)_4\{N(CH_2PCy_2)_3-\kappa^2P\}Ag]^+$, 1022 (95) $[W(CO)_3\{N(CH_2PCy_2)_3-\kappa^2P\}Ag]^+$.

2.11. X-ray crystallography

Table 1 provides a summary of the crystallographic data for compounds **5**, **6**, **8**, **9** and **11**. Data were collected using Oxford Diffraction Xcalibur PX Ultra (**5**, **8**, **9** and **11**) and Xcalibur 3 (**6**)

Table 1
Crystal data, data collection and refinement parameters for compounds **5**, **6**, **8**, **9** and **11**.^a

Data	5	6	8	9	11
Formula	$C_{27}H_{60}NP_3$	$C_{43}H_{72}MoNO_4P_3$	$C_{43}H_{72}AuClNO_4P_3W$	$C_{86}H_{144}Cl_2Mo_2N_2O_8P_6Pt$	$[C_{86}H_{144}AgN_2O_8P_6W_2](ClO_4)$
Solvent	–	–	–	$2CH_2Cl_2$	–
Formula weight	491.67	855.87	1176.19	2147.57	2094.87
Colour, habit	Colourless blocks	Colourless tablets	Colourless shards	Colourless blocks	Pale yellow plates
Crystal size (mm)	$0.24 \times 0.13 \times 0.11$	$0.42 \times 0.26 \times 0.10$	$0.28 \times 0.09 \times 0.07$	$0.28 \times 0.16 \times 0.07$	$0.26 \times 0.25 \times 0.10$
Temperature (K)	173	173	173	173	293
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pbca$ (no. 61)	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
<i>a</i> (Å)	11.51153(12)	15.11884(19)	11.01766(7)	14.15811(19)	12.70098(11)
<i>b</i> (Å)	15.27016(16)	12.87650(14)	17.61223(7)	14.1726(2)	26.2168(2)
<i>c</i> (Å)	37.7523(4)	23.4163(3)	12.96732(8)	24.9176(4)	14.79270(13)
α (°)	–	–	–	–	–
β (°)	–	106.5290(14)	111.2489(7)	91.1687(12)	107.2617(9)
γ (°)	–	–	–	–	–
<i>V</i> (Å ³)	6636.21(12)	4370.25(10)	2345.18(3)	4998.86(13)	4703.81(7)
<i>Z</i>	8	4	2	2 ^d	2 ^d
<i>D</i> _{calc} (g cm ⁻³)	0.984	1.301	1.666	1.427	1.479
Radiation used	Cu K α	Mo K α	Cu K α	Cu K α	Cu K α
μ (mm ⁻¹)	1.721	0.450	12.057	7.366	7.744
2θ max (°)	143	65	145	143	145
Number of unique reflections					
Measured (<i>R</i> _{int})	6386 (0.037)	14 259 (0.038)	7435 (0.028)	9721 (0.030)	8784 (0.024)
obs, $ F_o > 4\sigma(F_o)$	4477	11 350	7294	9004	7477
Number of variables	281	469	488	575	548
<i>R</i> ₁ (obs) ^b	0.038	0.039	0.030	0.027	0.036
<i>wR</i> ₂ (all) ^c	0.104	0.104	0.077	0.072	0.100

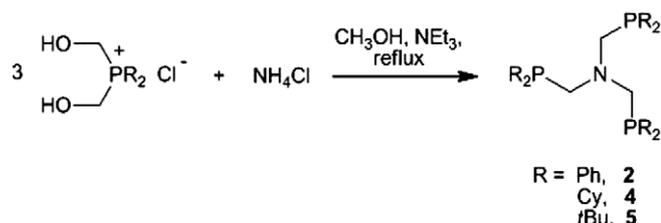
^a Details in common: graphite monochromated radiation, refinement based on F^2 .

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

^d The complex has crystallographic *C*_i symmetry.

diffractometers, and the structures were refined based on F^2 using the SHELXTL and SHELX-97 program systems [31]. The structure of **8** was shown to be a partial racemic twin by a combination of R -factor tests [$R_1^+ = 0.0342$, $R_1^- = 0.0370$] and by use of the Flack parameter [$\chi^+ = +0.366(9)$, $\chi^- = +0.634(9)$]; the lower residuals given in the table are from refinements where the Flack parameter was included as a variable.



Scheme 1. The formation of N-triphos ligands bearing diphenylphosphino (**2**), dicyclohexylphosphino (**4**) and *di*-*tert*-butylphosphino (**5**) via the phosphorus based Mannich-type reaction.

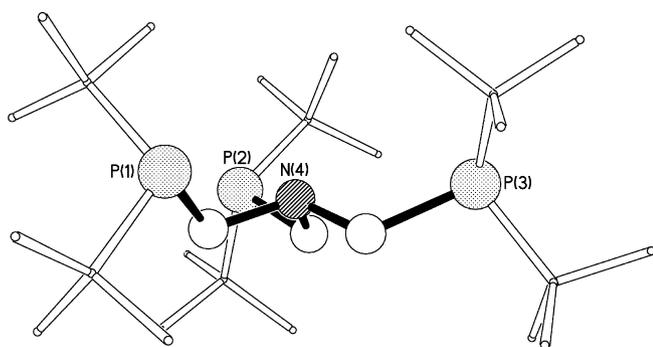


Fig. 1. The molecular structure of **5**.

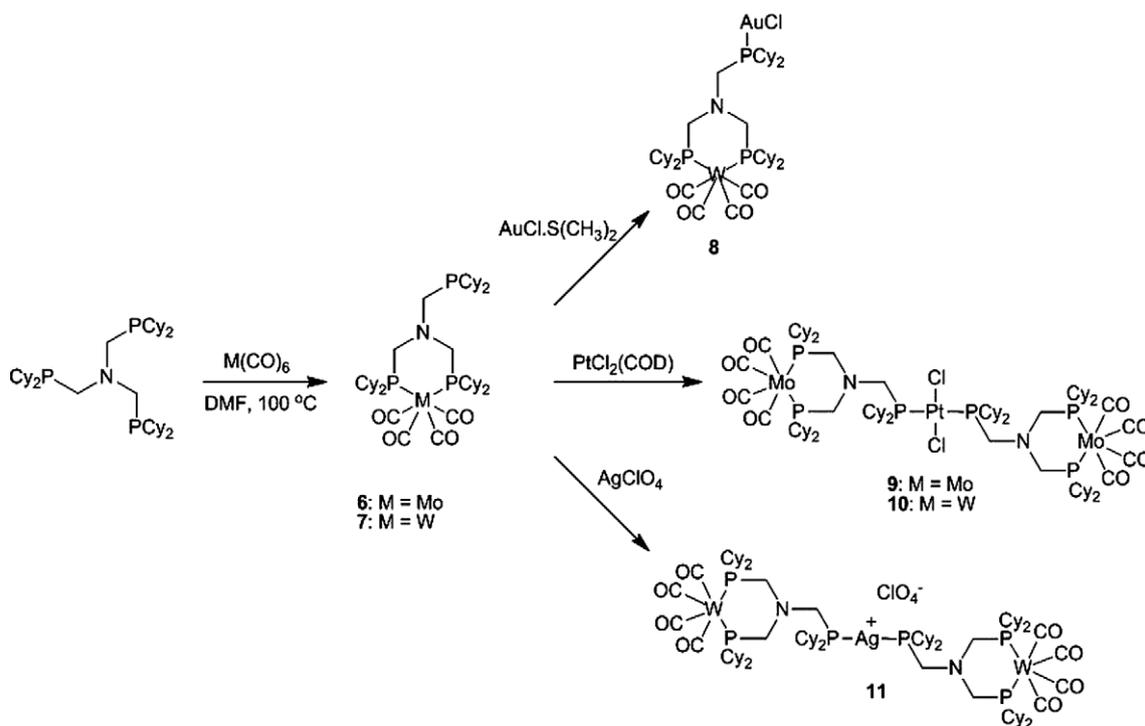
3. Results and discussion

3.1. Ligand synthesis

N-triphos ligands bearing diphenylphosphino, dicyclohexylphosphino and *di*-*tert*-butylphosphino groups were prepared by a modified procedure to that reported by Markl et al. [26]. The air stable diphenyl or dialkyl hydroxymethylphosphonium chloride salts were found to be particularly convenient starting materials and easily prepared via the reaction of the required secondary phosphine with 2 equiv of formaldehyde in the presence of hydrochloric acid [30]. The phosphonium chloride salts could be conveniently deprotonated *in situ*, using excess triethylamine, to the corresponding hydroxymethylphosphine and reacted in a phosphorus based Mannich condensation reaction [32–34] with ammonium chloride (Scheme 1). The N-triphos ligands **2** and **4** were conveniently isolated as white precipitates in high yield (>80%) after several hours at reflux by simply filtering off the methanol solvent. The *tert*-butyl ligand **5** was found to be much more soluble in methanol and was consequently isolated in lower yield (52%) as colourless crystals on recrystallisation from methanol. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra for **2** were consistent with literature data, while the $^{31}\text{P}\{^1\text{H}\}$ spectra for **4** and **5** gave single resonances at -17.0 and -12.5 ppm, respectively. The X-ray crystallographic structure of **5** (Fig. 1) revealed molecular threefold symmetry about the central bridgehead nitrogen atom with the bulky *tert*-butyl groups orientated away from each other.

3.2. Coordination chemistry

The cyclohexyl ligand **4** was selected for coordination chemistry investigations because of its high yielding synthesis and the greater availability of the dicyclohexylphosphine starting material. Tri-phos-type ligands are well known to chelate in a tridentate fashion and found to commonly occupy facial coordination sites



Scheme 2. Reaction of the dicyclohexylphosphine N-triphos ligand (**4**) with $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, followed by coordination of the free phosphine arm to form a series of heterometallic gold, platinum and silver complexes.

of octahedral, square pyramidal and trigonal bipyramidal metal centres [1]. Group 6 hexacarbonyls are widely used to react with phosphine ligands, via carbonyl displacement, and may be anticipated to form facially capping tricarbonyl complexes with triphosphines [20]. Reaction of equimolar amounts of **4** with $\text{Mo}(\text{CO})_6$ in DMF at 100°C (Scheme 2) gave the new complex $[\text{Mo}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3\text{-}\kappa^2\text{P}\}]$ (**6**). The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **6** showed resonances at 22.8 ppm and -16.7 ppm in an approximate 2:1 integration. This indicated that a bidentate complex had formed instead of the expected facially capping tricarbonyl complex. Two dicyclohexylphosphino arms of ligand **4** chelate to the Mo centre accounting for the higher frequency resonance at 22.8 ppm while the third arm remains uncoordinated which accounts for the lower frequency signal at -16.7 ppm. This was further supported by the IR spectrum complex **6** which showed a strong absorption at 2008 cm^{-1} and a broad peak with shoulders at 1888 cm^{-1} characteristic of a *cis*-tetracarbonyl complex [35]. Reaction of **4** with $\text{W}(\text{CO})_6$ under the same reaction conditions gave $[\text{W}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3\text{-}\kappa^2\text{P}\}]$ (**7**) which displayed a similar pattern in its $^{31}\text{P}\{^1\text{H}\}$ spectrum, showing a higher frequency chemical shift to 3.2 ppm, with ^{183}W satellites ($^1J = 217\text{ Hz}$), and a lower frequency resonance at -16.9 ppm accounting for the free phosphorus arm. The IR spectrum of this complex also indicated a tetracarbonyl complex while the LSIMS spectrum showed a characteristic pattern of carbonyl loss. Crystals of the Mo complex **6** suitable for X-ray diffraction were obtained by cooling a hot solution of **6** to ambient temperature. The molecular structure of **6** (Fig. 2) confirmed the tetracarbonyl and the expected six-membered chelate ring formed by the bidentate phosphine arms with a $\text{P}(1)\text{-Mo-P}(2)$ bite angle of $87.476(15)^\circ$ (Table 2). The space filling diagram (Fig. 3) shows the extent of the steric crowding around the metal centre as a result of the bulky dicyclohexylphosphine groups which clearly prevent the coordination of the third phosphine arm. Attempts to enforce coordination of the free arm by heating to reflux in DMF only resulted in recovery of the bidentate complex. Experiments under identical reaction conditions with the less sterically hindered triphos or N-triphos ligands exclusively produced the facial capping tridentate $\text{LMo}(\text{CO})_3$ or $\text{LW}(\text{CO})_3$ complexes and therefore confirm that steric

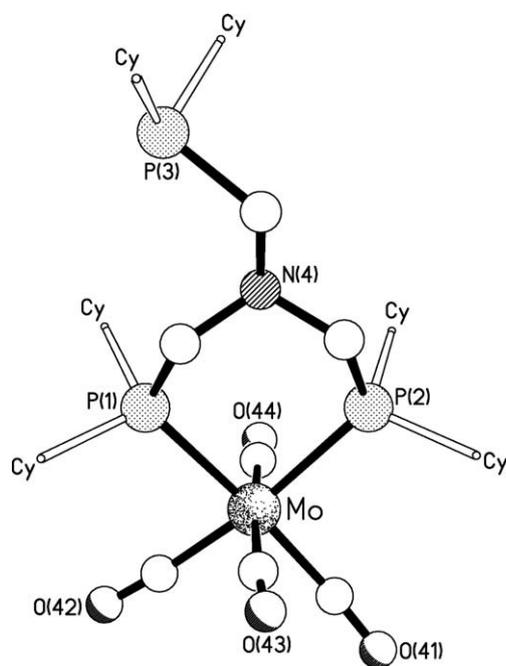


Fig. 2. The molecular structure of **6**. The cyclohexyl groups have been omitted and replaced with "Cy" for clarity.

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for **6** and **8**.

6		8	
Mo–P(1)	2.5145(5)	Au–Cl	2.2921(18)
Mo–P(2)	2.5303(5)	Au–P(3)	2.2370(16)
Mo–C(41)	1.987(2)	W–P(1)	2.5275(15)
Mo–C(42)	1.988(2)	W–P(2)	2.5218(16)
Mo–C(43)	2.040(2)	W–C(41)	2.022(7)
Mo–C(44)	2.045(2)	W–C(42)	1.988(7)
		W–C(44)	2.052(6)
		W–C(43)	2.044(6)
P(1)–Mo–P(2)	87.476(15)	Cl–Au–P(3)	178.12(6)
P(1)–Mo–C(41)	172.07(7)	P(1)–W–P(2)	88.42(5)
P(1)–Mo–C(42)	86.80(6)	P(1)–W–C(41)	178.2(2)
P(1)–Mo–C(43)	87.90(6)	P(1)–W–C(42)	94.7(2)
P(1)–Mo–C(44)	97.07(6)	P(1)–W–C(43)	95.5(2)
P(2)–Mo–C(41)	93.97(7)	P(1)–W–C(44)	88.1(2)
P(2)–Mo–C(42)	172.62(6)	P(2)–W–C(41)	90.4(2)
P(2)–Mo–C(43)	88.82(6)	P(2)–W–C(42)	176.8(2)
P(2)–Mo–C(44)	91.17(6)	P(2)–W–C(43)	97.64(19)
		P(2)–W–C(44)	89.9(2)

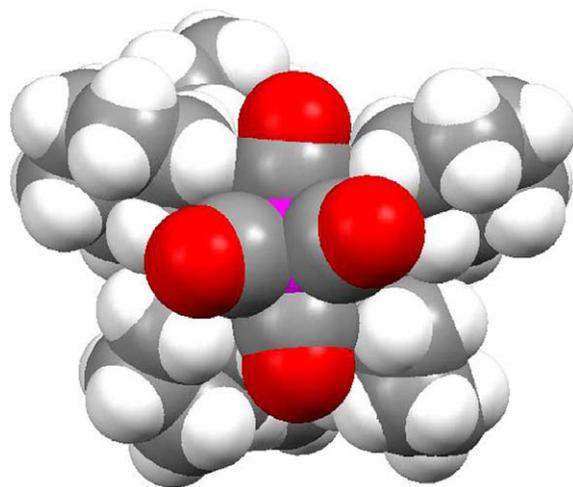


Fig. 3. Space-filling representation of **6** showing the steric bulk of the cyclohexyl groups around the $\text{Mo}(\text{CO})_4$ centre.

interactions prevent the third arm of ligand **4** from coordinating. The formation of bidentate triphos transition metal complexes, resulting in two bound and one free phosphorus donor, are rarer and generally dictated by the choice of metal cation and not by the steric constraints of the ligands [36–40]. Comparable bidentate complexes, using the triphos ligand, have been formed under mild reaction conditions using the precursor metal carbonyl complexes $([\text{M}(\text{CO})_4(\text{piperidine})_2])$ $\text{M} = \text{Mo}$ or W which contain two labile piperidine groups [41].

This steric control enforced by ligand **4** at the Mo and W metal centres, which results in a freely available phosphorus arm, presents a simple and straight forward route to the formation multi-metallic complexes using one simple ligand scaffold. To investigate the scope of coordination chemistry available to this free phosphine arm, complexes **6** and **7** were reacted with a range of transition metal salts (Scheme 2) with aim of preparing a series of heteromultimetallic complexes. Reaction of complex **7** with one equivalent $[\text{AuCl}(\text{SMe})_2]$ at room temperature for 2 h resulted in the formation of the mixed Au:W complex $[\text{W}(\text{CO})_4\{\text{N}(\text{CH}_2\text{PCy}_2)_3\text{-}\kappa^2\text{P}\}\text{AuCl}]$ (**8**). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** showed a characteristic high frequency shift of the uncoordinated phosphine arm from -16.9 ppm to 13.8 ppm on reaction with gold

chloride. Crystals suitable for single crystal analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **8** overnight. The molecular structure of **8** (Fig. 4) revealed the expected coordination of the lone dicyclohexylphosphine arm to gold chloride in a linear fashion, the Cl–Au–P(3) bond angle being 178.12(6)° with an Au–P(3) bond distance of 2.2370(16) Å (Table 2).

In an attempt to form a mixed trimetallic complex 2 equiv of the complex **6** or **7** were reacted with 1 equiv of [PtCl₂(COD)] in CH₂Cl₂ (Scheme 2). This resulted in the immediate precipitation of insoluble white solids that were found to be the bisligated species [[Mo(CO)₄{N(CH₂PCy₂)₃-κ²P}]₂(μ-PtCl₂) (**9**) and [[W(CO)₄{N(CH₂PCy₂)₃-κ²P}]₂(μ-PtCl₂) (**10**) based on their elemental analysis and LSIMS spectra which showed molecular ion peaks at 1977 *m/z* and 2153 *m/z*, respectively. The ³¹P{¹H} NMR spectrum of **9** (Fig. 5) showed resonances at 29.1 and 16.3 ppm, however the Pt–P coupling constant could not be resolved owing to its poor solubility and resulting low concentration in all solvents. Unfortunately complex **10** was found to be insoluble and ³¹P NMR could not be obtained. A small amount of crystalline solid of complex **9**, suitable for X-ray diffraction studies, was obtained when the filtrate of this reaction was allowed to slowly evaporate at room temperature over a period of 4 days. The molecular structure of **9** revealed an almost perfectly square planar platinum centre with the two bulky P(3) dicyclohexylphosphino groups in a *trans* configuration with Pt–P(3) bond distances of 2.3237(6) Å. The chelating *bis*-phosphino molybdenum moieties of the complex are oriented away from each other above and below the plane of the PtCl₂ centre, presumably for steric reasons.

Reaction of 2 equiv of the tungsten complex **7** with 1 equiv of AgClO₄ in DCM resulted in the formation the bisligated silver complex [[W(CO)₄{N(CH₂PCy₂)₃-κ²P}]₂(μ-Ag)ClO₄ (**11**) (Scheme 2). This complex was found to be non-labile on the NMR timescale at room temperature. The ³¹P{¹H} NMR spectrum of **11** (Fig. 6) displayed a distinctive ¹⁰⁷Ag,P, ¹⁰⁹Ag,P coupling pattern of two doublets centred at 13.8 ppm in addition to the low frequency

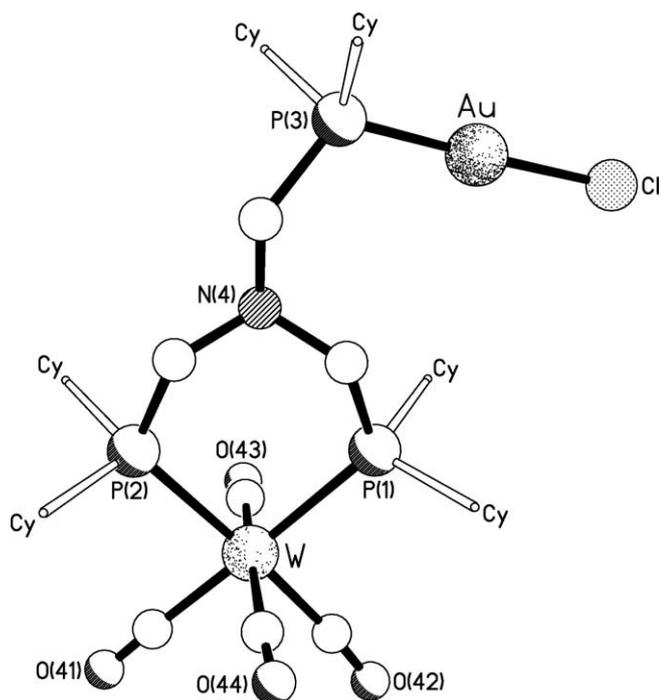


Fig. 4. The molecular structure of **8**. The cyclohexyl groups have been omitted and replaced with "Cy" for clarity.

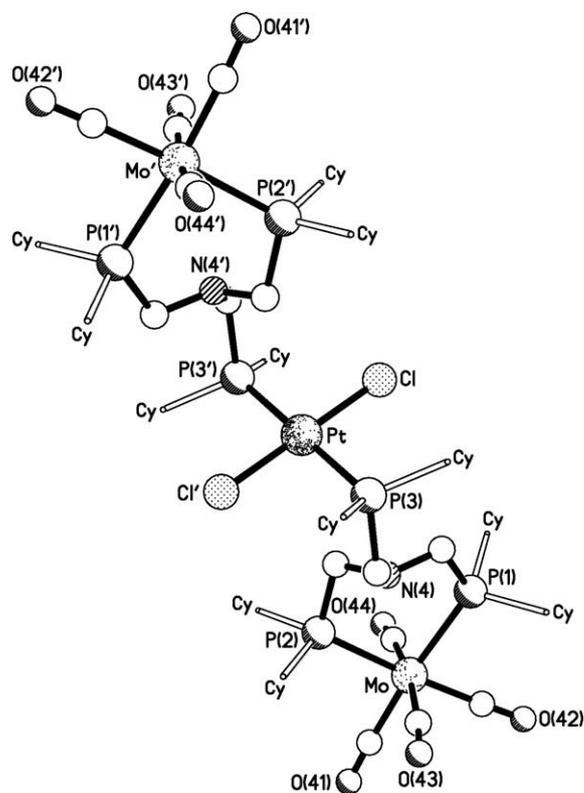


Fig. 5. The molecular structure of **9**. The cyclohexyl groups have been omitted and replaced with "Cy" for clarity.

resonance at 7.8 ppm for the chelating dicyclohexylphosphino arms of the complex. The magnitudes of the ¹J(¹⁰⁷Ag,P) and ¹J(¹⁰⁹Ag,P) coupling constants are a useful indicator of the coordination number at the metal centre [42]. In the case of complex **11** the ¹J(^{107/109}Ag,P) coupling constants were 460 and 503 Hz, respectively, which indicates that two phosphine groups are bonded to the silver centre. The structurally related complex [Ag(PCy₃)₂]O₃SCF₃, which is also non-labile on the NMR timescale at room temperature, displays similar ¹J(^{107/109}Ag,P) coupling constants of 463 and 534 Hz to that of **11** [43]. Single crystals of **11** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **11** over a period of 3 days. The molecular structure of **11** (Fig. 7) bears several similar features to that of complex **9**. The steric bulk of the two

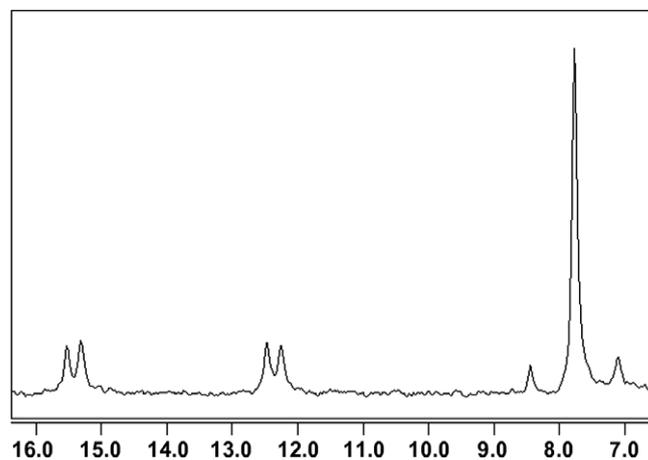


Fig. 6. The ³¹P{¹H} NMR spectrum of (**11**).

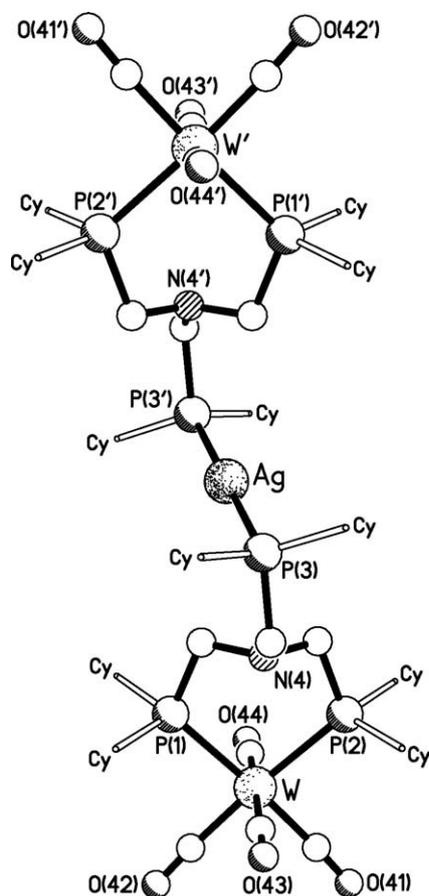


Fig. 7. The molecular structure of **11**. The cyclohexyl groups have been omitted and replaced with “Cy” for clarity.

opposing lone dicyclohexylphosphino arms P(3) results in a perfectly linear P(3)–Ag–P(3') arrangement at the silver centre with a bond angle of 180° (Table 3).

The three P–C–N–l.p. torsion angles can be used to describe the conformational changes in the solid state structures of the free ligand (**5**) and metal complexes **6**, **8**, **9** and **11**, where the lone pair on the nitrogen has been assumed to occupy the ‘empty’ tetrahedral site. An approximate gauche conformation can be seen for the free *tert*-butyl ligand **5** and also for complexes **6** and **8** (Table 3), whilst complexes **9** and **11** display an anti conformation for the non-chelating coordinated P(3) arm. The chelating phosphine arm P(2) of complexes **9** and **11** is syn, and the P(1) torsion angle is intermediate between gauche and syn in **9**, and approximately syn in complex **11**. This reflects the change in the orientation of the N–l.p. vector with respect to the proximal P₂M metal coordination plane (and consequently the N···M distance). In complexes **6** and **8** this vector is almost perpendicular to the plane, being inclined by ca. 87° and 77° respectively, with N···M separations of ca. 4.02 and 4.07 Å, respectively. In contrast, for complexes **9** and **11** the N–l.p. vector is inclined by only ca. 23° and 26°, respectively, to the P₂M plane, and the N···M distances are ca. 3.67 and 3.70 Å, respectively (Table 4).

4. Conclusions

We have reported the preparation of two new nitrogen centred cyclohexyl and *tert*-butyl triphosphine ligands via a general synthetic route that should allow the synthesis of a wide range of other N-triphos-type ligands bearing different phosphino groups.

Table 3
Selected bond lengths (Å) and angles (°) for **9** and **11**.

	9		11
Pt–Cl	2.3057(7)	Ag–P(3)	2.3814(10)
Pt–P(3)	2.3237(6)	W–P(1)	2.5399(10)
Mo–P(1)	2.5549(7)	W–P(2)	2.5497(10)
Mo–P(2)	2.5455(7)	W–C(41)	1.979(5)
Mo–C(41)	1.987(3)	W–C(42)	1.975(5)
Mo–C(42)	1.989(3)	W–C(43)	2.030(5)
Mo–C(43)	2.047(3)	W–C(44)	2.028(5)
Mo–C(44)	2.021(3)		
Cl–Pt–Cl'	180	P(3)–Ag–P(3')	180
Cl–Pt–P(3)	92.16(2)	P(1)–W–P(2)	92.18(3)
Cl–Pt–P(3')	87.84(2)		
P(3)–Pt–P(3')	180		
P(1)–Mo–P(2)	91.07(2)		

Table 4
The P–C–N–lone pair torsion angles (°) for **5**, **6**, **8**, **9** and **11**.

	5	6	8	9	11
P(1)–C(1)–N(4)–l.p.	–49.7	+38.9	–42.7	–34.7	+17.1
P(2)–C(2)–N(4)–l.p.	–53.0	–42.4	+45.1	+3.3	–11.1
P(3)–C(3)–N(4)–l.p.	–49.1	+52.3	–46.0	–173.6	+173.2

This method is limited only by the availability of the secondary phosphine starting material, however many secondary phosphines are now commercially available or reported in the literature by well described syntheses [44]. Our initial coordination chemistry studies using the cyclohexyl N-triphos ligand (**4**) have demonstrated that the steric bulk of this ligand dictates the type of complex that is formed. Bidentate Mo and W tetracarbonyl complexes were formed exclusively in preference to the expected facially capping tricarbonyl complexes which are common for triphos-type ligands. The resulting uncoordinated phosphorus arm was used to prepare a series of mixed bimetallic and trimetallic complexes that would otherwise be difficult to synthesise using less sterically bulky ligands. Bulky N-triphos ligands therefore present an interesting scaffold for the straightforward preparation of mixed metallic complexes by simple exploitation of the steric bulk. We are currently investigating the scope of this ligand and the *tert*-butyl triphos ligand for coordination to other transition metals, catalytic applications and the preparation of coordination polymers.

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Appendix A. Supplementary material

CCDC 744593–744597 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.017.

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