PAPER

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New d^4 dihydrides of Ru(IV) and Os(IV) with π-donor ligands: $M(H)_2(chelate)(P^iPr_3)_2$ with chelate = *ortho*-XYC_6H_4 with X, Y = O, NR; R = H or CH_3

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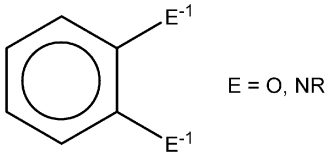
The synthesis and characterization of $Ru(H)_2$(*ortho*-$OC_6H_4E)L_2$ (L = P^iPr_3, E = NH, O) show these to be dihydrides with a nonoctahedral structure. The former compound reacts with H_2 to give $Ru(H)_3(OC_6H_4NH_2)L_2$, which has the ability to hydrogenate ^{t}BuHC=CH_2. Osmium analogs are available from $Os(H)_3ClL_2$, and the mono-*N*-methyl example $Os(H)_2[N(Me)C_6H_4NH]L_2$ shows inequivalent hydrides by ^{1}H NMR at 20 °C. It exchanges with D_2 faster into the NH site than into the OsH sites. Triflic acid protonates $Os(H)_2[N(Me)C_6H_4NH]L_2$ at the metal to give a trihydride. Catechol protonates $Os(H)_2[N(Me)C_6H_4NH]L_2$ to displace the *ortho*-diamine to give $Os(H)_2(OC_6H_4O)L_2$. The collective evidence is consistent with a dianionic, not a quinoid oxidation state for the chelate ligands and a d^4, six-coordinate potential energy surface, often with low barriers between alternative *non-octahedral* structures.

Introduction

Six-coordinate species of ruthenium and osmium in oxidation state +4 represent an interesting development, especially when they are unsaturated. Synthetic access to $M(H)_2Cl_2L_2$ (L = P^iPr_3) in recent years[1,2] was followed by an exploration of their reactivity towards alkynes (yielding carbenes and carbynes), as well as binding H_2 and catalytic alkene and alkyne hydrogenation.[3–11] The molecules $M(H)_2Cl_2L_2$ are exceptional in *not* being octahedral, but also in having the two bulky phosphines *cisoid* ($\angle$P–M–P ~112°). The actual structure has been deduced[2,12,13] to be a compromise between the conflicting dictates of the d^4 electronic configuration and the minimization of steric pressures and this feature of the d^4 configuration has recently been generalized.[14,15] In part because these are crowded molecules, reactivity can sometimes require heating (atypical for 16-electron species). Finally, because the +2 oxidation state is preferred (or at least very common) for Ru and Os, reactivity by reductive elimination can occur, most often by loss of HCl to a Brønsted basic reagent, if it is available.[12,16]

We report here the outcome of efforts to broaden the class of molecules $M(H)_2X_2L_2$ by incorporation of chelating *ortho* catecholates or diamides **A**. These permit further exploration of the unusual nonoctahedral structure of this class of compounds and, when the two donor groups E are not identical, provide further insight into the fluxionality of these molecules.



A

Experimental

General

All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Solvents were distilled from Na, Na/benzophenone, P_2O_5, or CaH_2, degassed prior to use, and stored over 4 Å molecular sieves in airtight vessels. Lithium salts *o*-$C_6H_4(OH)OLi$ and *o*-$C_6H_4(NH_2)OLi$ were prepared by reacting ^{n}BuLi with catechol (see below) and 2-aminophenol (1 : 1 molar ratio) in benzene, respectively, then isolated as white solids by removal of the volatiles *in vacuo*. $[RuHCl(P^iPr_3)_2]_2$,[17] written in this section as a monomer to clarify reaction stoichiometries, and $Os(H)_3Cl(P^iPr_3)_2$[18] were prepared as previously reported; all other reagents were used as received from commercial vendors. ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{31}P NMR spectra are referenced to an external standard of 85% H_3PO_4 (0 ppm). NMR spectra were recorded with either a Varian Gemini 2000 (300 MHz ^{1}H; 121 MHz ^{31}P; 75 MHz ^{13}C), a Varian Unity INOVA instrument (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C), or a Varian Unity INOVA instrument (500 MHz ^{1}H, 126 MHz ^{13}C). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, vt = virtual triplet, dvt = doublet of virtual triplets, m = multiplet, br = broad, ap = apparent. Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer.

***o*-C_6H_4(OH)OLi.** In a 100 ml Schlenk flask, 5.11 ml (8.18 mmol) of BuLi (1.6 M in hexane) was added *via* syringe to a solution of 0.9 g (8.18 mmol) catechol in 40 ml of benzene. White precipitate formed immediately. After stirring for another 0.5 h, the solvent was removed under reduced pressure. The white product was washed by hexane and dried *in vacuo*. IR: ν_{OH} 3487 cm^{-1}.

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$Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$. In a 100 ml Schlenk flask, 116 mg $C_6H_4(OH)OLi$ (1 mmol) was added to a solution of $RuHCl(P^iPr_3)_2$ (458 mg, 1 mmol) in 40 ml benzene. $C_6H_4(OH)OLi$ dissolved gradually and the resulting red brown solution was stirred for 14 h. The reaction mixture was then passed through a 1 cm plug of neutral alumina with benzene and taken to dryness. Yield: 480 mg (90%). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ − 13.63 (t, $^2J_{P-H}$ = 35 Hz, 2H Ru–H), 1.10 (dd, J_{P-H}=14 Hz, $^3J_{H-H}$ = 6.9 Hz, 36H, $P(CHMe_2)_3$), 2.18 (m, 6H, PCH), 7.06 (m, 2H, Ar–H), 7.53 (m, 2H, Ar–H). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 90.5 (s).

Isomerization of 1-pentene catalyzed by $Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$. A 5.0 mg (9.4 μmol) amount of $Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$ was dissolved in 0.5 ml of C_6D_6 in an NMR tube. *Via* syringe, 50 μl (0.46 mmol) of 1-pentene was added. The tube was fitted with a Teflon stopcock, shaken and heated to 55 °C. The sample was monitored periodically by ^1H and $^{31}P\{^1H\}$ NMR and showed only the signals of $Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$. ^1H NMR showed 94% conversion to 2-pentene in 80 h (*trans* : *cis* = 2.19 : 1).

$Ru(CO)_2(P^iPr_3)_2(OC_6H_4O)$. A solution of $Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$ (15 mg, 0.028 mmol) in C_6D_6 (0.5 ml) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and excess CO (1 atm.) was introduced into the tube. When the solution warmed to room temperature and the tube was shaken, the solution color immediately changed from deep red brown to pale yellow. ^1H and $^{31}P\{^1H\}$ NMR and IR spectra showed complete conversion to $Ru(CO)_2(P^iPr_3)_2(OC_6H_4O)$. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 1.17 (dvt, J_{P-H} = 6.3 Hz, $^3J_{H-H}$ = 7.2 Hz, 36H, $P(CHMe_2)_3$), 2.16 (m, 6H, $P(CHMe_2)_3$), 6.81 (m, 2H, Ar–H), 6.97 (m, 2H, Ar–H). The peak of free H_2 is observed at 4.50 ppm. $^{31}P\{^1H\}$ (121 MHz, C_6D_6, 20 °C): δ 43.4 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): δ 19.9 (s, $P(CHMe_2)_3$), 24.5 (vt, J_{P-C} = 9.4 Hz, $P(CHMe_2)_3$), 115.4 (s, Ar–C), 116.1 (s, Ar–C), 162.1 (s, Ar–C), 184.4 (CO). IR: ν_{CO} (benzene) 2014, 1945 cm^{-1}.

Synthesis of $Ru(H)_2(P^iPr_3)_2(O(3\text{-}CH_3)C_6H_3O)$. A solution of $RuHCl(P^iPr_3)_2$(20 mg, 0.044 mmol) in benzene-d_6 (0.5 ml) was placed in an NMR tube with a Teflon stopcock. Lithium 3-methyl-catecholate (5.6 mg, 0.044 mmol) was added and the tube was shaken. The lithium salt dissolved gradually. ^1H and $^{31}P\{^1H\}$ NMR showed complete conversion to $Ru(H)_2(P^iPr_3)_2(O_2C_7H_6)$ in 14 h. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ −13.74 (t, $^2J_{P-H}$ = 35.7 Hz, 2H Ru–H), 1.15 (dd, J_{P-H} = 13.5 Hz, $^3J_{H-H}$ = 7.2 Hz, 36H, $P(CHMe_2)$), 2.22 (m, 6H, $P(CHMe_2)$), 2.71 (s, 3H, CH_3–Ar), 6.97 (d, 1H, Ar–H), 7.03 (dd, 1H, Ar–H), 7.44 (d, 1H, Ar–H). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): 89.5 (s).

Synthesis of $Ru(H)_2(P^iPr_3)_2(OC_6H_4NH)$. In a 100 ml Schlenk flask, 115 mg (*o*)-$C_6H_4(NH_2)OLi$ (1 mmol) was added to a solution of $RuHCl(P^iPr_3)_2$ (458 mg, 1 mmol) in 40 ml toluene. (*o*)-$C_6H_4(NH_2)OLi$ dissolved gradually and the resulting red brown solution was stirred for 6 h. After separation of LiCl by filtration, the solution was taken to dryness. Yield: 488 mg (92%). ^1H NMR (300 MHz, C_7D_8, 20 °C): δ −11.46 (t, $^2J_{P-H}$ = 35 Hz, 2H, Ru–H), 1.05 (dd, $^3J_{P-H}$ = 13 Hz, $^3J_{H-H}$ = 6.8 Hz, 36H, $P(CHMe_2)_3$), 1.99 (m, 6H, $P(CHMe_2)_3$), 6.92 (t, 1H, Ar–H), 7.06 (t, 1H, Ar–H), 7.14 (d, 1H, Ar–H), 7.45 (d, 1H, Ar–H), 7.74 (s, 1H, N–H), $^{31}P\{^1H\}$ NMR (121 MHz, C_7D_8, 20 °C): δ 95.1 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_7D_8, 20 °C): 19.7 (s, $P(CHMe_2)_3$), 28.6 (vt, J_{P-C} = 11.4 Hz, $P(CHMe_2)_3$), 29.0 (vt, J_{P-C} = 11.5 Hz, $P(CHMe_2)_3$), 115.3 (s, Ar–C), 116.5 (s, Ar–C), 116.7 (s, Ar–C), 119.0 (s, Ar–C), 150.6 (s, Ar–C), 164.2 (s, Ar–C).

$RuH_3(P^iPr_3)_2(OC_6H_4NH_2)$. A solution of $Ru(H)_2(P^iPr_3)_2(OC_6H_4NH)$ (20 mg, 0.038 mmol) in C_7D_8 (0.5 ml) was placed in an NMR tube fitted with a Teflon stopcock. The solution was frozen in liquid N_2, the headspace was evacuated, and excess H_2 (1 atm.) was introduced into the tube. When the solution warmed to room temperature and the tube was shaken, the solution color changed from deep red brown to pale yellow in less than 1 h. ^1H and $^{31}P\{^1H\}$ NMR spectra showed complete conversion to $RuH_3(P^iPr_3)_2(OC_6H_4NH_2)$. ^1H NMR (300 MHz, C_7D_8, 20 °C): −12.39 (t, $^2J_{P-H}$ = 14.7 Hz, 3H, Ru–H), 1.05 (dd, $^3J_{P-H}$ = 11.7 Hz, $^3J_{H-H}$ = 6.3 Hz, 18H, $P(CHMe_2)_3$), 1.13 (dd, $^3J_{P-H}$ = 12.9 Hz, $^3J_{H-H}$ = 6.3 Hz, 18H, $P(CHMe_2)_3$), 1.76 (m, 6H, $P(CHMe_2)_3$), 4.34 (s, 2H, NH_2), 6.35 (m, 1H, Ar–H), 6.81 (d, 1H, Ar–H), 6.99 (m, 2H, Ar–H). $^{31}P\{^1H\}$ NMR (121 MHz, C_7D_8, 20 °C): δ 60.4 (s).

Synthesis of $(\eta^5\text{-}(o)\text{-}CH_3\text{-}C_6H_4O)RuH(P^iPr_3)_2$. A solution of $RuHCl(P^iPr_3)_2$ (20 mg, 0.044 mmol) in benzene-d_6 (0.5 ml) was placed in an NMR tube with a Teflon stopcock. Lithium 2-methylphenolate (5 mg, 0.044 mmol) was added and the tube was shaken. The lithium salt dissolved gradually and the solution color became lighter. ^1H and $^{31}P\{^1H\}$ NMR showed complete conversion to $(\eta^5\text{-}(o)\text{-}CH_3\text{-}C_6H_4O)RuH(P^iPr_3)_2$ in 14 h. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ −14.15 (ap t, $^2J_{P-H}$ = 37.5 Hz, 1H, Ru–H), 0.96 (dd, $^3J_{P-H}$ = 11.7 Hz, $^3J_{H-H}$ = 7.2 Hz, 9H, $P(CHMe_2)$, 1.02 (dd, $^3J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 6.6 Hz, 9H, $P(CHMe_2)$, 1.24 (m, 18H, $P(CHMe_2)$), 1.679 (m, 3H, $P(CHMe_2)$), 2.18 (s, 3H, Ar–CH_3), 2.27 (m, 3H, $P(CHMe_2)$), 3.85 (br, 1H, Ar–H), 4.66 (br, 1H, Ar–H), 5.20 (br, 1H, Ar–H), 5.58 (br, 1H, Ar–H). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 62.8 (s), 65.9 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 20 °C): δ 16.7 (s, Ar–CH_3), 20.4 (s, $P(CHMe_2)$, 20.7 (s, $P(CHMe_2)$), 21.0 (s, $P(CHMe_2)$), 21.7 (s, $P(CHMe_2)$), 28.1 (d, $^1J_{P-C}$ = 17.5 Hz, $P(CHMe_2)$), 29.0 (d, $^1J_{P-C}$ = 17.2 Hz, $P(CHMe_2)$), 67.8 (s, Ar–C), 75.8 (s, Ar–C), 91.3 (s, Ar–C), 97.8 (s, Ar–C), 101.4 (s, Ar–C), 165.5 (s, Ar–C).

Synthesis of $Os(H)_2(N(H)C_6H_4NH)(P^iPr_3)_2$. In an NMR tube, $Os(H)_3Cl(P^iPr_3)_2$ (0.01g, 0.018 mmol) and 1,2-phenylenediamine (0.004 g, 0.036 mmol) were dissolved in 0.5 ml of benzene-d_6. The reaction proceeds for 48 h and a white precipitate was observed (the corresponding hydrochloride salt of the amine reagent). After 48 h the solution had turned yellow-orange and the volatiles were removed under *vacuo*. The mixture consists of *ca.* equimolar amounts of the title compound and the amine hydrochloride. ^1H NMR (300 MHz, C_6D_6, 20 °C): −13.51 (t, $J_{(H-P)}$ = 38 Hz, Os–*H*, 2H), 1.00 (dvt, N = 19.2 Hz, Os–P(CH(CH_3)$_2$)), 1.97 (m, Os–P($CH(CH_3)_2$)), 7.11 and 7.44 (AA′MM′ system, 4H), 8.34 (br, Os–[N(*H*)C_6H_4N*H*], 2H). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 20 °C): 43.0.

Synthesis of $Os(H)_2(N(CH_3)C_6H_4NH)(P^iPr_3)_2$. The compound $Os(H)_3Cl(P^iPr_3)_2$ (0.1 g, 0.18 mmol) and *N*-methyl-1,2-phenylenediamine (44.4 μl, 0.36 mmol) were dissolved in 10 ml of benzene. After 30 min at room temperature *tert*-butylethylene (25 μl, 0.18 mmol) was added to the reaction mixture *via* syringe. The reaction was allowed to proceed for 24 h at room temperature. A white precipitate was observed to form in solution. The volatiles were removed under *vacuo* and the product was extracted with pentane (2 × 5 ml). The volatiles were removed under *vacuo* to produce a red solid. The ^1H NMR spectrum shows that this solid still contains some free amine. Several attempts to further purify the compound were unsuccessful. ^1H NMR (300 MHz, C_6D_6,

20 °C): −12.02 (t, $J_{(H-P)}$ = 35 Hz, Os–*H*, 1H), −13.67 (td, $J_{(H-P)}$ = 37 Hz, $J_{(H-H)}$ = 3 Hz, Os–*H*, 1H), 0.88 (dvt, N = 18.3 Hz, Os–P(CH(CH_3)$_2$)), 0.90 (dvt, N = 19.2 Hz, Os–P(CH(CH_3)$_2$)), 1.98 (m, Os–P(C*H*(CH$_3$)$_2$)), 4.41 (t, $J_{(H-P)}$ = 1.8 Hz, Os–[N(CH_3)C$_6$H$_4$NH], 3H), 7.10 (vt, $J_{(H-H)}$ = 7.4 Hz, aryl H, 1H), 7.21 (vt, $J_{(H-H)}$ = 7.2 Hz, aryl H, 1H), 7.41 (d, $J_{(H-H)}$ = 8.4 Hz, aryl H, 1H), 7.55 (d, $J_{(H-H)}$ = 8.4 Hz, aryl H, 1H), 8.85 (br, Os–[N(CH$_3$)C$_6$H$_4$N*H*], 1H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 54.8.

Synthesis of [OsH$_3$(N(Me)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$]$^+$ O$_3$SCF$_3^-$. In an NMR tube, Os(H)$_2$(N(CH$_3$)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$ (0.01g, 0.016 mmol) was dissolved in 0.5 ml of benzene-d$_6$ and triflic acid (0.7 µl, 0.016 mmol) was added to the solution *via* syringe. The reaction is instantaneous and the solution turned green-brown. The volatiles were removed under *vacuo* and a greenish residue was obtained. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −8.15 (td, $J_{(H-P)}$ = 16 Hz, $J_{(H-H)}$ = 3 Hz, Os–*H*, 3H), 0.70 (dvt, N = 21.9 Hz, Os–P(CH(CH_3)$_2$)), 0.75 (dvt, N = 21.9 Hz, Os–P(CH(CH_3)$_2$)), 1.72 (m, Os–P(C*H*(CH$_3$)$_2$)), 4.43 (s, OsN(CH_3)C$_6$H$_4$NH, 3H), 6.79 (m, aryl H, 2H), 7.02 (d, $J_{(H-H)}$ = 9 Hz, aryl H, 1H), 8.46 (d, $J_{(H-H)}$ = 9 Hz, aryl H, 1H), 14.65 (br, OsN(CH$_3$)C$_6$H$_4$N*H*, 1H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 41.8. ^{13}C {^{1}H} NMR (100 MHz, C$_6$D$_6$, 20 °C): 19.4 (s, Os–P(CH(*C*H$_3$)$_2$)), 29.5 (s, Os–P(*C*H(CH$_3$)$_2$)), 54.3 (s, OsN(*C*H$_3$)C$_6$H$_4$NH$_2$), 113.9, 123.0, 124.6, 125.9 (s, aryl C), 156.3, 158.9, (s, aryl *ipso*-C). ^{1}H NMR (300 MHz, d$_8$-THF, −85 °C): −8.03 (t, $J_{(H-P)}$ = 16 Hz, Os–*H*, 3H, $T_{1\ min}$ (−84 °C) = 85 ms).

Reaction of Os(H)$_2$(N(CH$_3$)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$ with catechol. In an NMR tube, Os(H)$_2$(N(CH$_3$)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$ (0.01 g, 0.016 mmol) and catechol (0.007 g, 0.064 mmol) were dissolved in 0.5 ml of toluene-d$_8$. After 5 min of mixing the reagents at room temperature, 5 mol% population of the compound [OsH$_3$(N(Me)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$]$^+$ is detected in the NMR tube, along with unreacted diamido compound and 1 mol% of Os(H)$_2$(OC$_6$H$_4$O)(P^{i}Pr$_3$)$_2$, the substitution product. When the reaction is allowed to proceed for 8 h, only traces of the cationic trihydrido compound remain and the major product is Os(H)$_2$(OC$_6$H$_4$O)(P^{i}Pr$_3$)$_2$. Vacuum removal of the volatiles under *vacuo* with constant heating does not remove the excess catechol or the released free amine. The substitution product was therefore extracted with portions of pentane, in which it is slightly soluble. Data for Os(H)$_2$(OC$_6$H$_4$O)(P^{i}Pr$_3$)$_2$: ^{1}H NMR (300 MHz, C$_7$D$_8$, 20 °C): −16.61 (t, $J_{(H-P)}$ = 36 Hz, Os–*H*, 2H), 1.01 (dd, $J_{(H-H)}$ = 13 Hz, $J_{(H-P)}$ = 8 Hz, Os–P(CH(CH_3)$_2$)), 2.14 (m, Os–P(C*H*(CH$_3$)$_2$)), 6.85 and 7.46 (AA′MM′ system, 4H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_7$D$_8$, 20 °C): 40.6. Only diagnostic data are given for the cation.

[OsH$_3$(η^2-N(CH$_3$)C$_6$H$_4$NH)(P^{i}Pr$_3$)$_2$]$^+$. ^{1}H NMR (300 MHz, C$_7$D$_8$, 20 °C): −8.26 (br.t, $J_{(H-P)}$ = 16 Hz, Os–*H*, 3H), 0.63 (br.m, Os–P(CH(CH_3)$_2$)), 1.60 (br.m, Os–P(C*H*(CH$_3$)$_2$)), 3.66 (s, OsN(CH_3)C$_6$H$_4$NH, 3H), 14.34 (s, OsN(CH$_3$)C$_6$H$_4$N*H*, 1H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_7$D$_8$, 20 °C): 42.1.

Synthesis of Os(H)$_2$(N(H)C$_6$H$_4$O)(P^{i}Pr$_3$)$_2$. In an NMR tube, Os(H)$_3$Cl(P^{i}Pr$_3$)$_2$ (0.01 g, 0.018 mmol) and lithium *o*-aminophenolate (0.0011 g, 0.018 mmol) were dissolved in 0.5 ml benzene-d$_6$. The reaction proceeds for 4 d at 70 °C and a white precipitate was observed. The volatiles are removed under *vacuo* and the product extracted with ether. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −14.72 (t, $J_{(H-P)}$ = 38 Hz, Os–*H*, 2H), 1.04 (dd, $J_{(H-H)}$ = 7.2 Hz, $J_{(H-P)}$ = 12.9 Hz, Os–P(CH(CH_3)$_2$)), 2.08 (m, Os–P(C*H*(CH$_3$)$_2$)), 6.97, 7.09, 7.33, 7.65 (t, t, d, d, respectively, $J_{(H-H)}$ = 6.3 Hz, aryl protons), 7.82 (br, Os–[N(*H*)C$_6$H$_4$O], 1H). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 41.4. The intermediate OsH$_3$(NH$_2$C$_6$H$_4$O)(P^{i}Pr$_3$)$_2$ is observed all through the reaction: ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −10.17 (br, Os–*H*, 1H),−13.54 (br, Os–*H*, 2H), 1.12 (dvt, N = 19.2 Hz, Os–P(CH(CH_3)$_2$)), 1.14 (dvt, N = 19.2 Hz, Os–P(CH(CH_3)$_2$)), 1.85 (m, Os–P(C*H*(CH$_3$)$_2$)), 5.06 (br, Os–[NH_2C$_6$H$_4$O], 2H), 6.39, 6.76, 7.00, 7.12 (t, d, t, d, respectively, $J_{(H-H)}$ = 6.3 Hz, aryl protons). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 30.7.

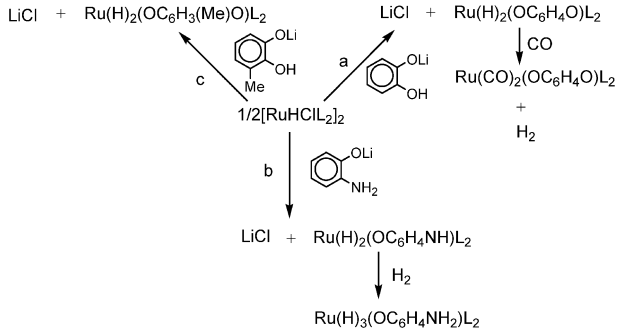
Synthesis of Os(H)$_2$(O(3-Me)C$_6$H$_3$O)(P^{i}Pr$_3$)$_2$. In an NMR tube, OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (0.01 g, 0.018 mmol) and lithium 3-methylcatecholate (0.0024 g, 0.018 mmol) were dissolved in 0.5 ml of benzene-d$_6$. The reaction proceeded for 18 h at 80 °C and a white precipitate was observed. The volatiles were removed under *vacuo*. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −17.17 (t, $J_{(H-P)}$ = 38 Hz, Os–*H*, 2H), 1.09 (dd, $J_{(H-H)}$ = 6 Hz, $J_{(H-P)}$ = 13 Hz, Os–P(CH(CH_3)$_2$), 2.21 (m, Os–P(C*H*(CH$_3$)$_2$)), 2.69 (s, aryl-CH_3, 3H), 6.90, 6.97, 7.01 (m, aryl protons, 3H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 37.8.

Synthesis of Os(H)$_2$(HN(3-Me)C$_6$H$_3$NH)(P^{i}Pr$_3$)$_2$. In an NMR tube, OsH$_3$Cl(P^{i}Pr$_3$)$_2$ (0.01 g, 0.018 mmol) and 2,3-diaminotoluene (0.0045 g, 0.036 mmol) were dissolved in 0.5 ml of benzene-d$_6$. The reaction was allowed to proceed at room temperature for 48 h. The mother liquor was decanted and separated from the white precipitate (hydrochloride salt of the amine reagent) formed during the reaction. ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): −13.52 (t, $J_{(H-P)}$ = 38 Hz, Os–*H*, 2H), 1.03 (dvt, N = 20 Hz, Os–P(CH(CH_3)$_2$)), 2.02 (m, Os–P(C*H*(CH$_3$)$_2$)), 2.55 (s, aryl-CH_3, 3H), 6.93, 7.07, 7.37 (d,t,d, $J_{(H-H)}$ = 8 Hz, aryl protons, 3H), 8.40 and 8.54 (each a brs, Os(N*H*(Me)C$_6$H$_3$N*H*, 1+1H). ^{31}P {^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 20 °C): 42.9.

X-ray structure determinations

(1) Ru(H)$_2$(OC$_6$H$_4$O)(P^{i}Pr$_3$)$_2$·C$_6$H$_6$. The selected crystal was affixed to the side of a glass fiber using silicone grease and cooled for data collection. The data were collected using 5 s frames with an omega scan of 0.30° on a Bruker SMART 6000 CCD. Examination of the lattice points using RLATT revealed that the crystal was twinned. An initial solution was obtained by using locally written software to integrate one of the two twin components. The Bruker Gemini software was then used to separate the two data sets. The crystal was twinned 180° about [001]. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. The structure was solved using SHELXTL and Fourier techniques. All hydrogen atoms were located and refined, including the hydrides. A final difference Fourier was essentially featureless with a maximum peak height of 0.87 e Å^{-3}.

(2) Os(H)$_2$(HNC$_6$H$_4$NMe)(P^{i}Pr$_3$)$_2$. The selected crystal fragment was affixed to a glass fiber using silicone grease and transferred to the Bruker SMART 6000 CCD system where it was cooled to 158 °C using a gas-flow cooling system of local design. The data were collected using 30 s frames with an omega scan of 0.30°. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. The structure was solved using SHELXTL and Fourier techniques. The structure consists of two independent molecules in the non-centrosymmetric space group $P2_1$; there was some concern about this space group assignment. The BMFIT program of Nyburg was used to compare the two independent molecules, and it was obvious that, while very similar, they are different due to a 60° twist of one P(i-Pr)$_3$ ligand. During refinement, it became apparent that the crystal chosen was also a racemic twin, so the refinement was completed using the SHELX series of programs, and the BASF



Scheme 1

value converged to 0.265(6). Hydrogen atoms were placed in fixed idealized positions for the refinement, and the hydrides were not located. A final difference Fourier map was essentially featureless, although there were several peaks over 1.00 e $Å^{-3}$ near the two metal atoms.

Results

$Ru(H)_2(OC_6H_4O)L_2$. Reaction of $[RuHClL_2]_2$ with singly-deprotonated catechol (1 : 1 Ru : catecholate) occurs over 14 h at 20 °C in benzene to produce a single product (Scheme 1, eqn. (a); the reaction rate is apparently limited by the low solubility of the lithium catecholate in benzene. NMR spectra in C_6D_6 serve to define the product stoichiometry. The hydride ligands appear as a sharp triplet (intensity 2H integrated *vs.* aryl *ortho* H), the aryl region shows only two chemical shifts (AA′XX′ pattern), and the ^{i}Pr methyls appear as a doublet of doublets; the implied lack of virtual coupling in the latter suggests that the phosphines are *not trans* (*i.e.*, $^2J_{PP'}$ is not large). The ^{31}P NMR spectrum is a singlet near 91 ppm, which compares well to the value[19] 103.2 ppm in $Ru(H)_2Cl_2(P^iPr_3)_2$.[20]

The presence of equimolar added catechol detectably alters the spectral parameters of $Ru(H)_2(OC_6H_4O)L_2$ in benzene at 20 °C. The hydride chemical shift moves 0.3 ppm downfield, and δ (^{31}P) moves 2 ppm downfield. Both aryl proton δ values of added catechol move downfield (0.2 and 0.4 ppm compared to catechol in benzene), but they are not coalesced with those of coordinated catecholate. Since the hydroxyl proton δ values of added catechol move downfield 2.9 ppm, the collective spectral data are consistent with hydrogen bonding between $Ru(H)_2(OC_6H_4O)_2L_2$ and catechol.

Table 1 Crystal data

Empirical Formula	$C_{30}H_{54}O_2P_2Ru$	$C_{25}H_{52}N_2OsP_2$
Color of crystal	orange	orange
Space group	$P\bar{1}$	$P2_1$
a	11.224(2)	8.9882(3)
b	11.907(2)	21.8475(9)
c	12.510(2)	14.1438(6)
α	77.529(5)	90
β	89.453(5)	97.4220(10)
γ	76.548(5)	90
Z	2	4
V/Å^3	1586.60	2754.14(19)
ρ_{calcd}/g cm^{-3}	1.276	1.526
T/K	−118	113
λ/Å	0.71073	0.71073
$R(F_o)^a$	0.0351	0.0322
$R_w(F_o)^b$	0.0346	0.0698

^{a} $R = \sum ||F_o| - |F_c|| \Big/ \sum |F_o|$

^{b} $R_w = \left[\sum w(|F_o| - |F_c|)^2 \Big/ \sum w|F_o|^2\right]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$

Table 2 Selected bond distances (Å) and angles (°) for $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$

RU(1)	H(1)	1.56(5)	
RU(1)	H(2)	1.39(6)	
RU(1)	P(10)	2.2833(15)	
RU(1)	P(20)	2.2876(14)	
RU(1)	O(2)	2.027(3)	
RU(1)	O(9)	2.031(3)	
O(2)	C(3)	1.348(6)	
O(9)	C(8)	1.350(6)	
C(3)	C(4)	1.389(7)	
C(3)	C(8)	1.406(6)	
C(4)	C(5)	1.382(8)	
C(5)	C(6)	1.376(8)	
C(6)	C(7)	1.362(8)	
C(7)	C(8)	1.392(7)	
P(10)	RU(1)	P(20)	114.39(5)
P(10)	RU(1)	O(2)	152.75(10)
P(10)	RU(1)	O(9)	87.22(10)
P(20)	RU(1)	O(2)	86.21(10)
P(20)	RU(1)	O(9)	151.58(10)
O(2)	RU(1)	O(9)	80.51(13)
RU(1)	O(2)	C(3)	112.9(3)
RU(1)	O(9)	C(8)	112.9(3)
P(10)	RU(1)	H(1)	66.0(17)
P(10)	RU(1)	H(2)	78.6(23)
P(20)	RU(1)	H(1)	78.2(16)
P(20)	RU(1)	H(2)	66.4(24)
O(2)	RU(1)	H(1)	139.1(17)
O(2)	RU(1)	H(2)	95.2(24)
O(9)	RU(1)	H(1)	95.7(17)
O(9)	RU(1)	H(2)	139.5(24)
H(1)	RU(1)	H(2)	112.(3)

Structure of $Ru(H)_2(P^iPr_3)_2(OC_6H_4O)$. This structure (Tables 1 and 2)† is remarkable for being non-octahedral. As seen in Figs. 1 and 2, the planes of Ru and any two identical ligands are neither orthogonal, nor coplanar, as would be true in an octahedron. Even considering only the heavier atoms, which are more accurately determined than the hydrides, the RuP_2 and the RuO_2 planes are neither orthogonal nor coplanar. This structure thus bears a remarkable similarity to that of $M(H)_2Cl_2(P^iPr_3)_2$ (M = Ru[19] and Os[1]), and it was reasoned there[2,12,13] that the observed structure was a compromise between the nonoctahedral structure dictated *electronically* for a d^4 six-coordinate species and the steric dictates of P^iPr_3 in conflict with chloride. Those arguments thus also pertain here, even if they force the two bulky phosphines into a small ∠P–Ru–P (114.4°) and even though the catecholate ligand has a small bite angle (∠O–Ru–O = 80.5°). Note, however, that the Cl–Ru–Cl angle in $Ru(H)_2Cl_2(P^iPr_3)_2$ is also only 84.3° indicating that the chelate ring constraint naturally meets the angle preferred even by monodentate ligands. The molecule has an idealized C_2 axis bisecting the PRuP angle and the ORuO angle, and there is no evidence for an *ortho* quinone structure in the aryl ring C/C distances. The catecholate chelate ring involving Ru is essentially planar (interior angles sum to 539° *vs.* 540° for planar), and the two Ru–O distances are indistinguishable (2.03 Å), and considerably shorter than to

† CCDC reference numbers 245545 and 245546. See http://www.rsc.org/suppdata/nj/b4/b411487f/ for crystallographic data in .cif or other electronic format.

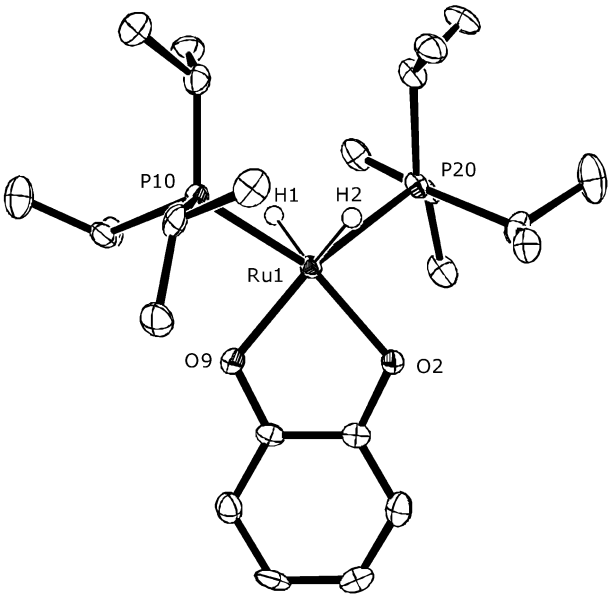
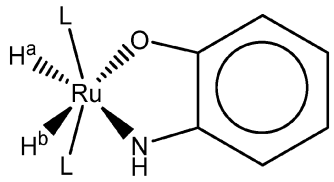


Fig. 1 ORTEP drawing (50% probability ellipsoids in all figures) of $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$ with H on C deleted, showing selected atom labeling. The idealized C_2 axis is vertical.

those in phenoxide oxygen in *cis*-RuH(O-tolyl)$(PMe_3)_4$,[21] where Ru–O is 2.152(3) Å and ∠Ru–O–C is 133.3°.

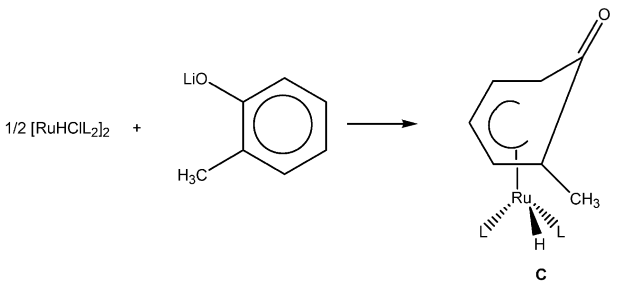
Comparison of this structure to that[22] of $Os(H)_2(OCH_2CF_3)_2(P^iPr_3)_2$ is instructive (Os and Ru have negligibly different covalent radii). Bond lengths and angles in this molecule are remarkably similar to those in $Ru(H)_2(OC_6H_4O)L_2$. The angle O–Os–O, at 81.0°, suggests that there is no major chelate constraint in the catecholate, and the similarity in the "twisted" orientation of the $M(H)_2$, $M(O)_2$ and MP_2 planes suggests that the competition between steric and electronic factors reaches the same equilibrium even with different metals and different alkoxides. This structural similarity also extends to $Os(H)_2X_2(P^iPr_3)_2$ where $X = OSO_2CF_3$ [22] or Cl.[1]

$Ru(H)_2[OC_6H_4(NH)]L_2$. Reaction of $[RuHClL_2]_2$ with the monolithium salt of *ortho*-aminophenol in benzene at 20 °C proceeds to completion within 6 h to give only one product (Scheme 1, eqn. (b)). This shows four aryl protons and *one* NH proton (7.7 ppm, broad), together with a hydride triplet; the latter integrates for two protons. The second hydride (*cf.* $[RuHClL_2]_2$ reagent) thus results from migration of one H from N to Ru; the reaction is oxidative addition. The ^{i}Pr groups show *one* diastereotopic ^{1}H NMR methyl chemical shift. These do not show virtual coupling, which suggests ∠P–Ru–P is significantly less than 180°. The ^{31}P NMR spectrum shows equivalent phosphines, and these become a triplet when only the hydrides are permitted to couple to P; this further supports the *di*hydride formulation. This is confirmed by the $T_{1\,min}$ (300 MHz, −75 °C) value of 226 (±4) ms. These data are consistent with structure **B**, provided some fluxional process effects site exchange of H^a and H^b, which are inequivalent in this structure(*syn vs. anti* to O). These hydrides remain a single ^{1}H NMR triplet at −85 °C in toluene-d_8.



B

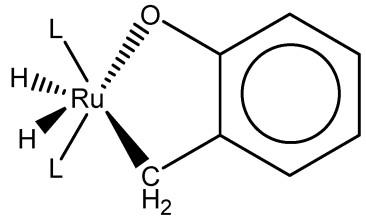
C–H Cleavage?[23] Given the occurrence of N–H oxidative addition above, we considered the possibility of an analogous reaction for a benzylic C–H bond. This reaction (eqn. (1)) proceeds to completion within 14 h at 20 °C in benzene, and the only observed product has the expected elemental composition, but four resonances of the aryl protons are sufficiently far upfield (3.8–5.6 ppm) to be diagnostic of a π-arene structure, and the benzylic protons integrate for 3 H.



C (1)

The single hydride ligand is an apparent triplet, but the individual broad components are equally consistent with a doublet of doublets structure. The two phosphine ligands are *in*equivalent, but separated by only ~3 ppm. This inequivalence arises from the methyl substituent, which destroys mirror symmetry for the molecule, leaving it chiral, and thus with inequivalent phosphines. The ^{i}Pr methyls appear as *four* chemical shifts, and without virtual coupling.

These spectral parameters are numerically very similar to those already reported[24] for $(\eta^5\text{-}C_6H_5O)RuH(PPh_3)_2$. In sum, forming a saturated η^5-cyclohexadienoyl product is preferred to forming **D**. Heating **C** for 2 h in benzene at 60 °C gives only partial decomposition, but no **D**. Carrying out the reaction of eqn. (1) at 50 °C in benzene for 1 h also gives only **C**.



D

Reactivity: (a) CO and 1-pentene. Reaction of $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$ with CO (1 atm.) is complete in time of mixing at 22 °C in benzene to give only *cis*, *trans*-$Ru(CO)_2(OC_6H_4O)(P^iPr_3)_2$, identified by ^{1}H and ^{31}P{^{1}H} NMR spectra (C_{2V} symmetry) and its two CO stretching frequencies. The

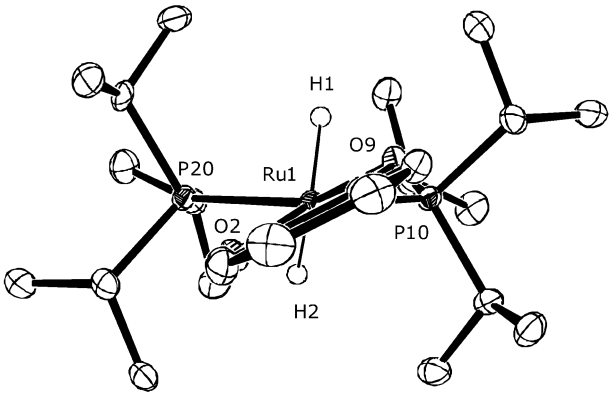
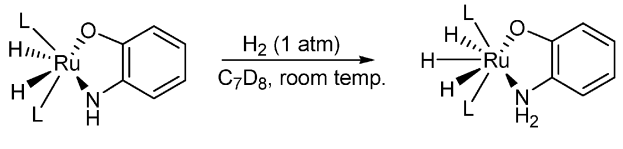


Fig. 2 ORTEP drawing of $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$ viewed down the idealized C_2 axis.

speed of this reaction is consistent with "operational unsaturation"[25–27] of the metal center, and the loss of H_2 consistent with the π-basicity of Ru being dominated by the arrival of the π-acidic carbonyl ligands; that is depletion of metal reducing power by two CO triggers conversion of 2 H^- to H_2.

While $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$ is unchanged by 1-pentene, the terminal olefin is isomerized to *trans*- and *cis*-2-pentene over 80 h at 55 °C. This olefin thus can bind to the complex, but only to a kinetically significant, rather than a detectable (NMR) extent.

(b) Hydrogenation and catalysis. Molecular hydrogen (1 atm.) fails to react with $Ru(H)_2(OC_6H_4O)(P^iPr_3)_2$ in C_6D_6 during 10 h at 20 °C. In contrast, $Ru(H)_2(OC_6H_4NH)(P^iPr_3)_2$ reacts with H_2 (1 atm.) readily in toluene-d_8 to generate a pale yellow solution in less than 1 h (eqn. (2)).



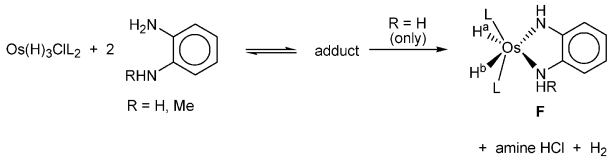
(2)

The complete conversion to product is confirmed by the appearance of a new ^1H NMR triplet at −12.39 ppm (intensity 3H integrated *vs.* aryl *ortho* H) as well as the appearance of a broad singlet at 4.34 ppm (intensity 2H integrated *vs.* aryl *ortho* H), the latter assigned as NH_2. Diastereotopic ^{i}Pr methyl hydrogens are also observed for the molecule, at 1.05 and 1.13 ppm. $^{31}P\{^1H\}$ NMR reveals a singlet at 60.4 ppm. All these are consistent with the formation of an 18-electron Ru(IV) complex with the structure **E**.[28] The hydride signal becomes broad at 50 °C in toluene-d_8, but there is only incomplete decoalescence by 90 °C. The value of T_1 goes through a minimum at 70 °C and 300 MHz, and the value 45[29,30] (±1) ms is too long to involve an H_2 ligand; a trihydride formulation with a small ∠H–Ru–H is thus indicated.

This reactivity towards H_2 enables catalytic olefin hydrogenation. If ^{t}BuHC=CH_2 in C_6D_6 at 20 °C is treated with H_2 (1 atm.) in the presence of 5 mol% $Ru(H)_2(OC_6H_4NH)L_2$, all hydrogen (the limiting reagent) is consumed within 2 h, with conversion of olefin to neohexane. The olefin is clearly capable of "dehydrogenation" of $RuH_3(OC_6H_4NH_2)L_2$ because, under the hydrogen-poor conditions at the end of this catalytic reaction, the only metal complex observed to be present is $Ru(H)_2(OC_6H_4NH)L_2$; 50% of the charged olefin remains unreacted due to the limited H_2 available.

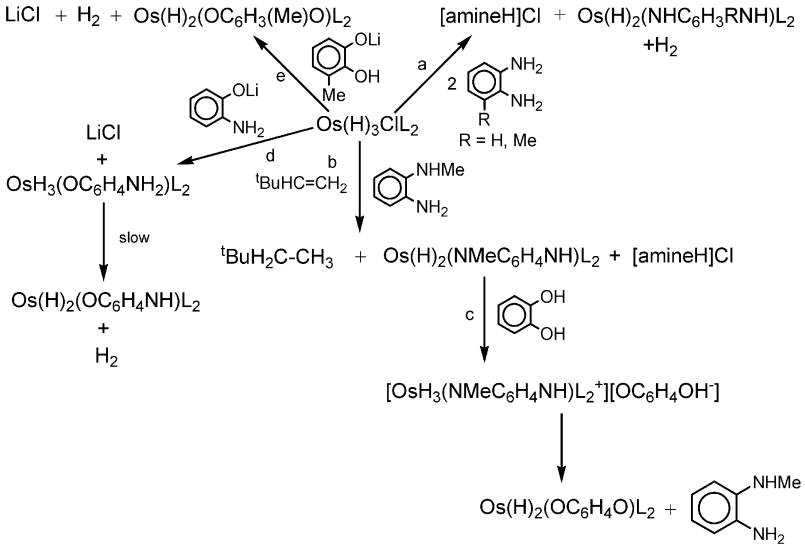
Osmium analogs. In an effort to develop greater electron richness (and thus reducing power) at the metal, we moved from Ru to Os, and from a catecholate to a diamide ligand. Since "$OsHClL_2$" is not synthetically available, we employed, as our OsL_2 source, the more hydrogen-rich $Os(H)_3ClL_2$. Since this Os source has a higher oxidation state than that in our Ru reagent, this has impact on the synthetic method, as well as the primary product formed.

(a) Phenylenediamine. We investigated the reaction (Scheme 2, eqn. (a)) of this osmium reagent with 1,2-phenylenediamine (1 : 2 stoichiometry) in benzene-d_6. The primary product is an adduct formed by these two reagents (eqn. (3)), characterized in the ^1H NMR by a very broad peak in the hydride region at −15.69 ppm, a very broad peak at 3.98 ppm (due to ArNH_2) and a very broad peak in the $^{31}P\{^1H\}$ NMR at 36.1 ppm.



(3)

No decoalesced ^1H NMRsignals for bound and free amine (*i.e.* excess) are observed at 22 °C in this solution, and the phosphine methyl proton region displays only one apparent quartet, indicating a dissociative equilibrium (eqn. (3)). Nevertheless, some of the final product $Os(H)_2(NHC_6H_4NH)(P^iPr_3)_2$ is already present in the reaction mixture within 1 h after mixing. After 24 h the reaction is complete, including precipitation of a colorless salt, the amine hydrochloride. The dihydride $Os(H)_2(NHC_6H_4NH)(P^iPr_3)_2$ is characterized in the ^1H NMR by a single triplet of intensity two at −13.51 ppm in the hydride region, two intensity two multiplets in the aryl region and a broad peak at 8.33 ppm due to bound NH groups. The ^{i}Pr methyl region displays one apparent quartet, indicating equivalent methyls. The single hydride peak and the absence of diastereotopic methyl groups indicate that this molecule is (time averaged) mirror-symmetric. The $^{31}P\{^1H\}$ NMR spectrum is a singlet at 43 ppm. We assign these signals to species **F** which shows that the second mole of amine serves to remove HCl.



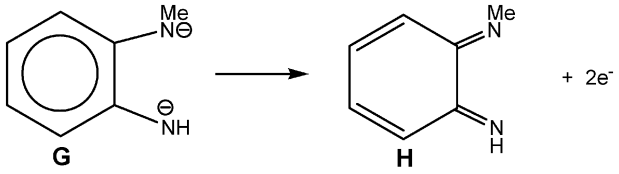
Scheme 2

(b) *N*-Methylphenylenediamine. Synthesis and characterization. The reaction of $Os(H)_3Cl(P^iPr_3)_2$ with *N*-methyl-1,2-phenylenediamine is additionally revealing (Scheme 2, eqn. (b) and also eqn. (3)). When the reaction is carried out in 1 : 2 stoichiometry (Os : amine) in benzene-d_6 an adduct is instantaneously and essentially completely formed (by ^1H and $^{31}P\{^1H\}$ NMR). This adduct is characterized by a broad singlet in the ^1H NMR spectrum at −14.44 ppm. Free and coordinated amine show coalesced ^1H NMR signals. The chemical shift of the methyl group and the amino protons shift downfield by 0.1 ppm and 1 ppm, respectively, the latter a singlet at 3.80 ppm. The relative magnitude of these shifts indicate that the donor group interacting with the metal center is the primary amine, NH_2. The aromatic protons of the amine have also shifted from their values for the pure arene in benzene. The phosphine methyl region ^1H NMR displays one apparent quartet, indicating a fast equilibrium. The $^{31}P\{^1H\}$ NMR displays a broad singlet at 27.0 ppm. Under these reaction conditions, no further change is observed over 24 h, and heating the reaction mixture to 55 °C for 17 h does *not* produce a significant amount of any other product. However, upon addition of 1 equivalent of *tert*-butylethylene, the reaction proceeds further at 25 °C and the conversion is complete after 24 h, producing the new compound $Os(H)_2(N(Me)C_6H_4NH)(P^iPr_3)_2$. Production of *neo*-hexane (hydrogenated olefin) is stoichiometric and a white precipitate is observed, presumably the corresponding chloride salt of the amine reagent. Two signals at −12.02 and −13.67 ppm, the former a triplet and the latter a triplet of doublets (due to coupling to two phosphines *and coupling to NH*, confirmed by selective NH decoupling) characterize the final product in the hydride region of the ^1H NMR spectrum. The N*Me* group and N*H* proton resonate as a broad triplet at 4.41 ppm and as a broad singlet at 8.85 ppm, respectively. Four signals are observed in the aryl region with the expected multiplicities and relative intensities for an *ortho*-C_6H_4XY ring, and diastereotopic apparent quartets are observed in the methyl phosphine region. The $^{31}P\{^1H\}$ NMR displays a singlet at 54.8 ppm. This is consistent with structure **F**, but, in contrast to the Ru analogs, the barrier to any mutual site exchange between inequivalent hydrides (H^a and H^b in eqn. (3)) is higher.

Intrigued by the large (11 ppm) difference in the $^{31}P\{^1H\}$ chemical shift between these two seemingly similar analogs, $Os(H)_2(N(Me)C_6H_4NH)(P^iPr_3)_2$ ($\mathbf{F^{Me}}$) and $Os(H)_2(N(H)C_6H_4NH)(P^iPr_3)_2$ ($\mathbf{F^H}$), we investigated the ^1H NMR spectra of compound $\mathbf{F^{Me}}$ at low temperatures to detect any possible C–H agostic interaction involving the *N*-methyl group in $\mathbf{F^{Me}}$. The ^1H NMR signals of compound $\mathbf{F^{Me}}$ suffer no significant transformation in the range from 20 °C to −70 °C. Moreover, the value of the C–H coupling constant of the methyl substituent remains constant over this range of temperatures ($J_{(C-H)} = 132$ Hz as measured from the ^{13}C satellites in the ^1H NMR), indicating a typical non-distorted sp^3 hybridized carbon. We also sought to detect a dynamic process (hydride site exchange) for compound $\mathbf{F^{Me}}$. The two distinct hydride signals show broadening at 60 °C, the signal at −13 ppm no longer showing resolvable coupling to the NH proton. Broadening is also observed for the *N*-methyl signal and the N–H signal, but no coalescence of the hydrides occurs. Compound $\mathbf{F^{Me}}$ does not decompose at 60 °C over 14 h in toluene-d_8.

Operationally unsaturated $Os(H)_2(N(Me)C_6H_4NH)(P^iPr_3)_2$ does not react with 1 atm. CO (in contrast to $Ru(H)_2(OC_6H_4)(P^iPr_3)_2$) or C_2H_4 at 20 °C in benzene, or with equimolar PhC≡CH (20 °C, benzene).

Molecular structure. Given (eqn. (4)) that the chelate ligand **G** has a redox alternative[31–34] form (**H**) that would leave Os in oxidation state +2, we determined the structure of $\mathbf{F^{Me}}$.



(4)

We were also interested in how structurally different are the NMe and NH groups in their bonds to Os and to the phenyl rings. Figs. 3 and 4 are chosen to allow comparison to Figs. 1 and 2. These reveal (Table 3) a similar overall structure, but the planar diamidobenzene ligand is twisted more from the OsP_2 plane, perhaps dictated by NMe-to-P^iPr_3 repulsions. This twist, if it originates from the methyl group, could be the origin of the 11 ppm different ^{31}P NMR chemical shifts for these two Os complexes. Probably as a consequence of this twist, the P–Os–P angle is 3° *larger* than the P–Ru–P angle.

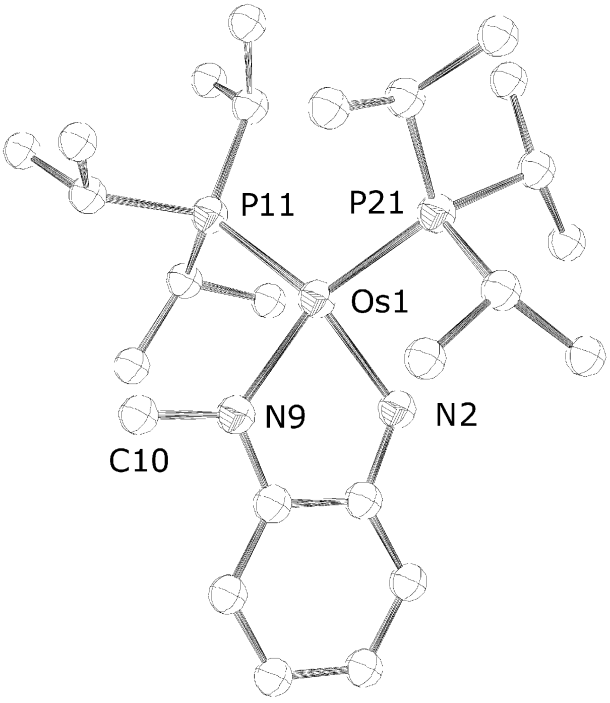


Fig. 3 ORTEP drawing of the non-hydrogen atoms of one molecule of $Os(H)_2(HNC_6H_4NMe)(P^iPr_3)_2$, oriented as in Fig. 1. Hydrides were not located in this X-ray study.

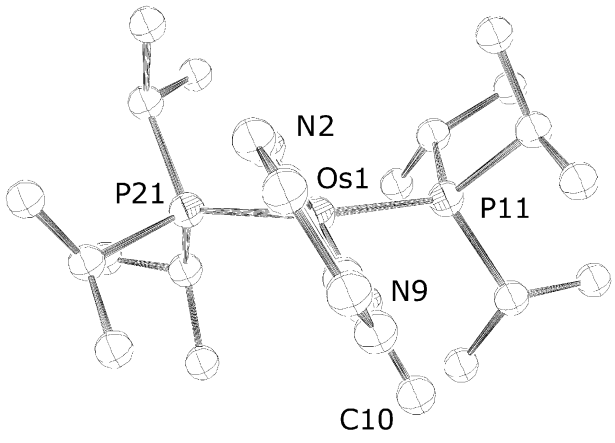
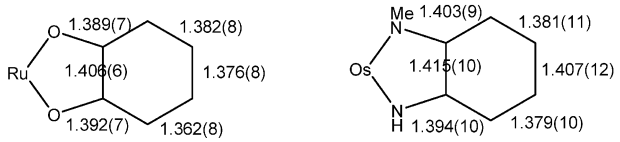


Fig. 4 ORTEP drawing of $Os(H)_2(HNC_6H_4NMe)(P^iPr_3)_2$, oriented as in Fig. 2. This molecule is approximately the enantiomer of the Ru complex in Fig. 2.



Scheme 3 Comparison of arene ring C–C distances.

The N–Os–N angle, at 76.7°, is nearly 4° *smaller* than the O–Ru–O angle (80.5°). The Os–NMe distance, 2.041 Å, is longer than the Os–NH distance, 2.003 Å. The three angles around the MeN9 sum to 360°, indicative of planarity. Carbon–carbon distances in the aryl ring show some weak evidence for the diimino form (**H**), especially in contrast to the ruthenium catecholate (Scheme 3). However, the best criterion to choose between forms **G** and **H** is the O–C or N–C distances.[35,36] By this criterion both ligands here (*i.e.* the Ru and Os compounds in Scheme 3) are in their fully reduced, dianionic form.

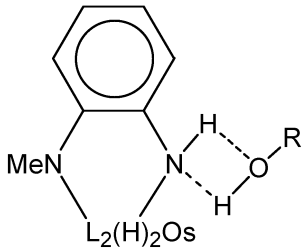
A recent study[35] of $Os(H)_2(OC_6H_4NH)(PPh_3)_2$, which also shows this same distortion away from octahedral geometry, also concluded that this contains Os(IV) and a dianionic chelate ligand. In contrast, the $RuCl_2(OC_6H_4NH)(PPh_3)_2$ analog has an *octahedral* geometry; a ground state with Ru(III) strongly spin-coupled to a radical monoanion chelate was deduced. Thus, the $Os(H)_2$ moiety is more reducing than the $RuCl_2$ unit.

(c) Reactivity of $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$ with protons. Triflic acid protonates compound $\mathbf{F^{Me}}$ in arene solvents at room temperature, to form the triflate salt of $[Os(H)_3(N(CH_3)C_6H_4NH)(P^iPr_3)_2]^+$ (**I**). The metal in $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$ is thus more basic than either nitrogen. A triplet of doublets (coupling to 2P and one N*H*) in the hydride region characterizes cation **I** in the ^1H NMR at −8.15 ppm. The methyl protons and the amide proton resonate as a singlet at 4.43 and a broad singlet at 14.65 ppm, respectively. Selective decoupling of the amido signal induces a multiplicity change in the hydride signal to a triplet, confirming that the doublet structure in the hydride peak is due to coupling to the amido proton. Complicated multiplets are observed in the aryl region, which are completely resolved into two triplets and two doublets when the solvent is d_8-THF, and the diastereotopic P-methyl groups appear as overlapping apparent quartets. The ^{19}F NMR chemical shift indicates no interaction of the triflate with the cation, and the $^{31}P\{^1H\}$ NMR spectrum is a singlet.

Due to the symmetry of the diamido ligand, the three hydride atoms cannot be chemically equivalent, even though we observe one sharp signal at 20 °C. In an attempt to decoalesce the hydrides, we investigated the low temperature properties of compound **I** in d_8-THF. Neither the hydride nor the NH proton signals in the ^1H NMR spectra undergo a significant change from 20 °C to −110 °C. The $^{31}P\{^1H\}$ NMR signal remains unchanged in the same range of temperatures. Relaxation rate measurements of the hydride ligands give a $T_{1\,min.}$ of 85 ms at −84 °C, confirming a trihydride formulation with $\angle H\text{–}Os\text{–}H < 90°$. This protonation with a strong acid helps to understand the following reaction with catechol.

(d) Substitution reactions on $Os(H)_2(N(CH_3)C_6H_4NH)(P^iPr_3)_2$. The above evidence for hydrogen bonding between $Ru(H)_2(OC_6H_4O)L_2$ and added catechol suggests that weak *acids* might replace the chelated diamide from Os. We therefore investigated a substitution reaction (Scheme 2, eqn. (c)) in toluene-d_8 at room temperature with excess catechol (1 : 4, Os : catechol). Within (5 min) the time of acquiring the first NMR spectrum, a broadening of the NH proton in compound $\mathbf{F^{Me}}$ was observed. This we attribute to hydrogen bonding between catechol and the NH proton of $\mathbf{F^{Me}}$. The only product detected at this stage is the catecholate salt of $[Os(H)_3(N(CH_3)C_6H_4NH)(P^iPr_3)_2]^+$ (**I**). The spectroscopic features of this compound are similar to the triflate salt of **I**, though not identical, thus indicating minor differences due to counterion identity. After 2 h, the substitution product $Os(H)_2(OC_6H_4O)(P^iPr_3)_2$ (**IV**) is observed (^1H, $^{31}P\{^1H\}$ NMR). The hydride region of the ^1H NMR spectrum displays a triplet at −16.61 ppm. The aryl region displays two multiplets and the P-methyl region displays one doublet of doublets, confirming the presence of two fold symmetry in the molecule. The $^{31}P\{^1H\}$ NMR spectrum of compound **IV** is a singlet at 40.6 ppm.

To prove that the most exchangeable site is the amide nitrogen, MeOD was added in excess to a solution of $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$. The NH proton signal immediately disappeared from the ^1H NMR spectrum and there was no intensity decrease in the OsH signal after 10 min at 22 °C. Given the hydrogen bonding evident between $Ru(H)_2(OC_6H_4O)L_2$ and catechol,[37–39] we suggest that this selective exchange of MeOD with the NH proton occurs *via* a structure such as **J**.



J

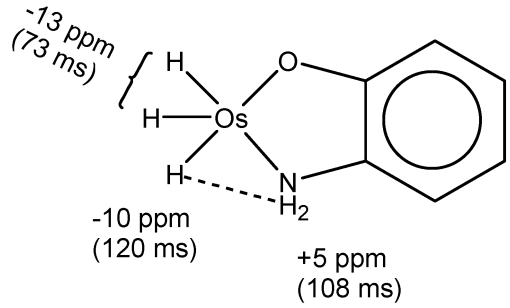
Reactivity towards H_2 and D_2. NMR spectra are unchanged over 24 h when compound **I** is subjected to 1 atm. of H_2 in C_6D_6 at room temperature. Under 1 atm. of D_2, deuterium is first incorporated in the NH signal after 10 min, and incorporation into the hydride positions is complete after 4 h. No further reactivity is observed in this solution at room temperature or at 70 °C for 24 h by ^2H NMR (*e.g.*, no free amine or $OsD_6(P^iPr_3)_2$ is observed). This result proves that compound **I** does bind H_2 (D_2), but in an unfavorable equilibrium at 1 atm. H_2 (solubility $\sim 10^{-3}$ M).

(e) Synthesis of $Os(H)_2(NHC_6H_4O)(P^iPr_3)_2$. To continue the study of six-coordinate d^4 osmium complexes with chelating ligands, we decided to study a more strongly asymmetric ligand, one bearing *ortho* alkoxide and amido donor substituents. The compound $Os(H)_3Cl(P^iPr_3)_2$ reacts very slowly with the lithium salt of *ortho*-aminophenolate at room temperature in benzene-d_6 (Scheme 2, eqn. (d)). At 70 °C, the reaction proceeds faster, and after 4 d the product obtained is $Os(H)_2(NHC_6H_4O)(P^iPr_3)_2$. The ^1H NMR spectrum of this molecule shows a triplet in the hydride region at −14.72 ppm, two doublets and two triplets in the aryl region, and a broad singlet at 7.82 ppm corresponding to the NH amido proton. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet. The ^1H NMR in the methyl phosphine region displays only one doublet of doublets, in agreement with the fact that we only observe one chemical shift for the hydride ligands. Nevertheless, any compound with such ligand distribution has chemically inequivalent hydrides and diastereotopic methyl groups (as observed for $Os(H)_2(NHC_6H_4NMe)(P^iPr_3)_2$). These results indicate there must exist a dynamic process that renders the two hydrides equivalent, and that the barrier for this process is lower when the chelate NMe is replaced by O.

During the course of the reaction at or above 20 °C, the intermediate $OsH_3(OC_6H_4NH_2)(P^iPr_3)_2$ is observed by ^1H and $^{31}P\{^1H\}$ NMR. This intermediate is characterized in the ^1H NMR spectrum by two unstructured signals at −10.7 and

−13.54 ppm in relative intensities 1 : 2, respectively. This behavior is analogous to that of compounds of general formula $OsH_3Cl(NR_3)(P^iPr_3)_2$ at −20 °C or below.[40] The aryl region of the ^1H NMR spectrum displays two doublets and two triplets; the NH_2 protons resonate at 5.06 ppm as a broad singlet and the phosphine region shows diastereotopic methyl signals. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet. Free H_2 is also observed during the reaction at room temperature (at higher temperature, it is lost rapidly to the head space).

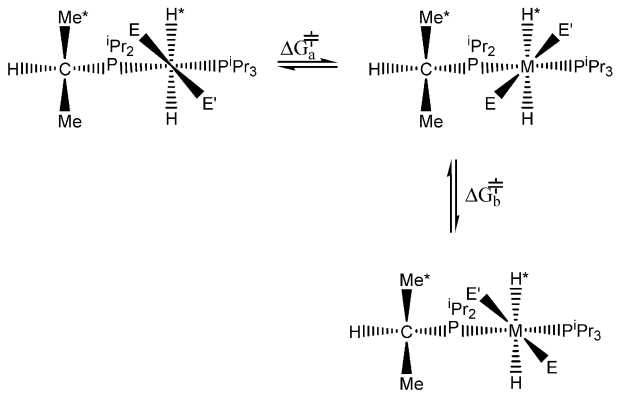
The hydride region of $OsH_3(OC_6H_4NH_2)(P^iPr_3)_2$ persists as two signals, 1 : 2 intensity, down to −70 °C, but *each* shows triplet structure between −40 °C and −70 °C. There is additional broadening of the intensity 2 hydride signal from −70 °C to −90 °C, and the minimum T_1 values (300 MHz, and generally at −80 ± 5 °C) are shown in **K**, together with a proposed assignment. None of these is short enough (< 10 ms) to indicate an H_2 ligand, but the 73 ms value indicates an acute H–Os–*H* angle. Note also the short value for the NH_2 protons. The 108 and 120 ms values are suggestive of mutual approach, and mutual dipole relaxation; for this reason, we suggest a hydrogen bond between them. These hydride values are all short compared to that measured (235 ms) here for the classical hydrides in $Os(H)_2(OC_6H_4NH)(P^iPr_3)_2$. Intramolecular hydrogen bonding illustrated in **K** can explain the lack of rapid site exchange of one of the three hydrides.



K

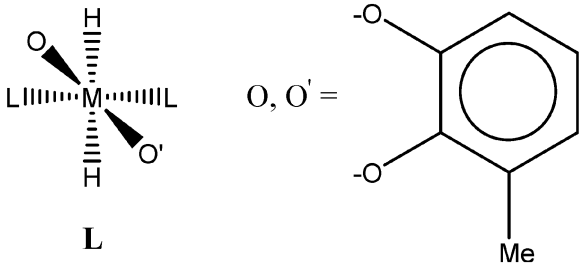
Interestingly, the unsaturated $Os(H)_2(NHC_6H_4O)(P^iPr_3)_2$ does *not* produce $OsH_3(NH_2C_6H_4O)(P^iPr_3)_2$ under equimolar amounts of H_2 in toluene-d_8 after 4 h at 20 °C. The added free H_2 is observed as a singlet at 4.5 ppm in the ^1H NMR spectrum. The absence of reactivity indicates that the two species are not yet at equilibrium during the course of the synthesis, but that the trihydride is the primary product, and it only slowly (20 °C) loses H_2, with loss of one amine H.

Fluxionality (Scheme 4). The equivalent hydrides seen even at low temperature for $M(H)_2(OC_6H_4NH)(P^iPr_3)_2$ could be accounted for by the typically facile site exchange of hydrides (*e.g.*, facile bond angle distortion and possible conversion to a rapidly rotating H_2 ligand). We were, however, puzzled by the lack of inequivalent (*i.e.*, diastereotopic) ^{i}Pr methyls in $M(H)_2(OC_6H_4NH)L_2$ (M = Ru and Os). Fluxional process **a** *alone* (involving heavy atom motion of the E/E′ chelate) cannot account for the observations; it makes the two hydrides equivalent, as well as Me and Me* equivalent, but it leaves the two phosphines inequivalent. Process **b** *alone* is unable to create time-average equivalence of all the sites observed to be equivalent; it leaves the hydrides inequivalent. However, *both* processes, the equivalent of full 180° rotation of the plane of the chelate ligand, must occur rapidly for $M(H)_2(OC_6H_4NH)L_2$.



Scheme 4

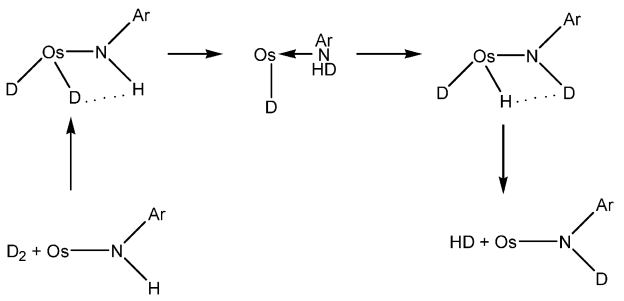
To test whether the above observations of a single ^{i}Pr methyl chemical shift might be due to *two* cases of accidental degeneracy (Ru and Os), we synthesized a more subtly asymmetric example for both metals **L** (Scheme 1, eqn. (c) and Scheme 2, eqn. (e)). For M = Ru, the resulting molecule



L

shows equivalent hydrides and one ^{i}Pr methyl ^1H NMR chemical shift, and one $^{31}P\{^1H\}$ NMR chemical shift. For M = Os, the heterogeneous reaction of $LiOC_6H_3(CH_3)OH$ with $Os(H)_3ClL_2$ proceeds in benzene, without any detectable intermediate, to give the Os example of **L** which shows equivalent hydrides, one ^{i}Pr methyl ^1H NMR chemical shift, and one $^{31}P\{^1H\}$ NMR chemical shift. In sum, the likelihood of accidental degeneracy of three sites in four different molecules is so low that we conclude the *two* fluxional processes in Scheme 4 occur rapidly at 20 °C for the 3-methyl catecholates of *both* Ru and Os.

To test whether the frozen fluxionality of $Os(H)_2(HNC_6H_4NMe)(P^iPr_3)_2$ is due to sterics (Me preventing rotation) or electronics (E = O *vs.* NR), we investigated the molecule containing the 2,3-diamidotoluene ligand. Reaction of $Os(H)_3Cl(P^iPr_3)_2$ with excess 2,3-diaminotoluene (1 : 2 stoichiometry) in benzene-d_6 (Scheme 2, eqn. (a)) proceeds spontaneously at room temperature to form an amino adduct, analogously to all the amines previously described (eqn. (3)). This adduct is characterized by a broad hydride signal at −14.29 ppm in the ^1H NMR spectrum and a broad peak at 25.9 ppm in the ^{31}P $\{^1H\}$ NMR spectrum. No decoalesced signals due to coordinated and free amine are observed, and only one chemical shift is present in the methyl phosphine region of the ^1H NMR spectrum. After 10 min some diamido product is already observed. After 48 h the reaction is complete and a substantial amount of white precipitate is observed in the reaction mixture (hydrochloride salt of the amine reagent). The final dihydrido diamido product is characterized in the ^1H NMR



Scheme 5

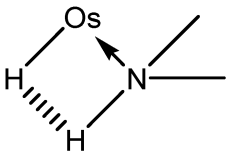
spectrum by a triplet in the hydride region at −13.51, *two* amido proton signals at 8.54 and 8.40 ppm, a singlet at 2.55 corresponding to the benzylic methyl, one apparent quartet in the ^{i}Pr methyl phosphine region and the corresponding aryl signals. The ^{31}P {^{1}H} NMR spectrum displays a sharp singlet at 42.9 ppm. Thus, we can conclude that this molecule is also fluxional. In conclusion, only for $Os(H)_2(NMeC_6H_4NH)L_2$ is the barrier higher and we suggest that this is due to steric conflicts between NCH_3 and P^iPr_3 in process **a** of Scheme 4.

Discussion

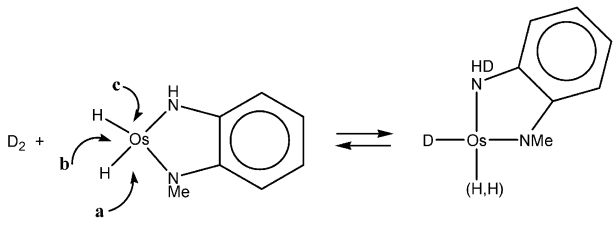
The synthetic methods employed here show similarities, but also fundamental differences. The fact that both involve oxidative addition of O–H or N–H bonds testifies to the considerable reducing power of Ru and Os (even if they are unsaturated) in an environment devoid of π-acid ligands (*e.g.*, CO). The difference is that the Ru examples introduce the chelate as an anion, by chloride metathesis. Certain of the Os cases in Scheme 2 employ neutral amine, with excess amine effecting reductive elimination of HCl; variable amine basicity can influence the success of this dehydrochlorination. Because the osmium source, $Os(H)_3ClL_2$ contains two more hydrides per metal than does "$RuHClL_2$", only Os involves loss of H_2 (eqn. (3)). The osmium reactions begin because unsaturated $Os(H)_3ClL_2$ has enough Lewis acidity to bind aryl amines.

$$Os(H)_2(chelate)L_2 + D_2 \rightleftharpoons OsH_2D_2(chelate)L_2 \qquad (5)$$

We suggest that intramolecular hydrogen bonding[41] (**M**) can be a more favorable source of evolved H_2 than would be reductive elimination from an $Os(H)_2$ substructure. The observed deuteration of NH as the most rapid isotope exchange in eqn. (5) supports the importance of coordinated D_2 in hydrogen bonding to the NHAr ligand (Scheme 5).



M



N

Scheme 6

The selectivity of this H/D exchange with D_2, being faster with N–H than with Os–H protons, demands that the effective binding site for D_2 to Os (Scheme 6) is at **c**, not **a** or **b** (these latter would effect deuteration of Os–H in a pentagonal bipyramidal intermediate). In addition, D_2 at site **c** must reversibly form deuterido/amine complex **N** (where the notation (H,H) leaves open the question of whether these are two hydrides, or H_2) at a rate faster than Os–D in **N** exchanges with (H,H).

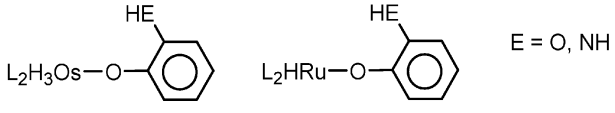
These experiments permit some comparisons of Ru *vs.* their Os analogs.

Table 3 Selected bond distances (Å) and angles (°) for two independent molecules of $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$

Os(1)	N(2)	2.004(5)	
Os(1)	N(9)	2.041(6)	
Os(1)	P(21)	2.2843(16)	
Os(1)	P(11)	2.3035(15)	
N(2)	C(3)	1.385(9)	
C(3)	C(4)	1.394(10)	
C(3)	C(8)	1.415(10)	
C(4)	C(5)	1.379(10)	
C(5)	C(6)	1.407(12)	
C(6)	C(7)	1.381(11)	
C(7)	C(8)	1.403(9)	
C(8)	N(9)	1.376(9)	
N(9)	C(10)	1.460(9)	
Os(31)	N(32)	1.998(6)	
Os(31)	N(39)	2.045(6)	
Os(31)	P(51)	2.2892(16)	
Os(31)	P(41)	2.3079(16)	
N(32)	C(33)	1.370(10)	
C(33)	C(34)	1.391(10)	
C(33)	C(38)	1.412(11)	
C(34)	C(35)	1.390(11)	
C(35)	C(36)	1.366(13)	
C(36)	C(37)	1.382(12)	
C(37)	C(38)	1.421(10)	
C(38)	N(39)	1.371(10)	
N(39)	C(40)	1.455(9)	
N(2)	Os(1)	N(9)	76.7(2)
N(2)	Os(1)	P(21)	96.45(17)
N(9)	Os(1)	P(21)	131.58(15)
N(2)	Os(1)	P(11)	132.04(16)
N(9)	Os(1)	P(11)	100.74(16)
P(21)	Os(1)	P(11)	117.22(6)
C(3)	N(2)	Os(1)	119.4(5)
C(8)	N(9)	Os(1)	117.2(5)
C(10)	N(9)	Os(1)	127.3(5)
N(32)	Os(31)	N(39)	76.5(2)
N(32)	Os(31)	P(51)	96.58(17)
N(39)	Os(31)	P(51)	130.26(16)
N(32)	Os(31)	P(41)	133.35(16)
N(39)	Os(31)	P(41)	100.87(16)
P(51)	Os(31)	P(41)	117.18(6)
C(33)	N(32)	Os(31)	120.1(5)
C(38)	N(39)	Os(31)	116.6(5)
C(40)	N(39)	Os(31)	127.7(5)

(1) Chloride replacement by a mono lithium catecholate succeeds not only for the chloride bridged $Ru_2(H)_2(\mu\text{-}Cl)_2(P^iPr_3)_4$ but also for the more hydride rich $Os(H)_3Cl(P^iPr_3)_2$, where H_2 loss occurs.

(2) The analogous reactions occur for *ortho*-amine phenoxide. The intermediates **O** and **P** are suggested, and the next step must be H–E bond cleavage.

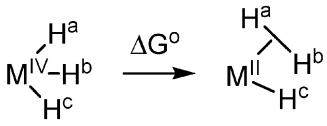


O **P**

For Ru, this directly furnishes the observed product, but the suggested RuH_3 intermediate is not detected. For Os, the intermediate $OsH_3(OC_6H_4NH_2)(P^iPr_3)_2$ *is* detected, and it only slowly loses H_2 at 70 °C. The Ru analog of this molecule, $RuH_3(OC_6H_4NH_2)(P^iPr_3)_2$, can be synthesized by addition of H_2 (1 atm.) to unsaturated $Ru(H)_2(OC_6H_4NH)(P^iPr_3)_2$, a net heterolytic splitting of H_2. The H_2 *adducts* of

$Os(H)_2(EC_6H_4E')L_2$ are thermodynamically unfavorable even under 1 atm. H_2, and the lack of observation of these in the amine reactions (Scheme 2, eqn. (a)) originates in their different mechanism *vs.* the lithium phenoxide reactions.

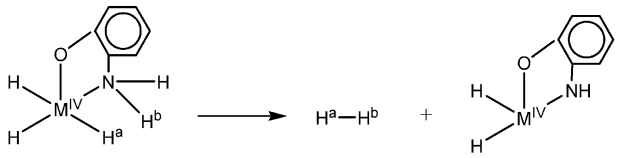
(3) The species $MH_3(OC_6H_4NH_2)(P^iPr_3)_2$ show a dramatic difference: for M = Os, the hydrides are not fully coalesced into a single ^1H NMR signal (being instead a 2 : 1 intensity pattern), while for M = Ru the hydrides show site exchange averaging even at −70 °C. Other examples are known where rearrangement barriers are higher for 5d than for 4d analogs.[42,43] In addition, *if* the mechanism of site exchange involves a η^2-H_2 intermediate (eqn. (6)),



(6)

then the energetics of reduction of M would typically have a larger ΔG° for M = Os than for Ru.

(4) The H_2 loss process from $MH_3(OC_6H_4NH_2)(P^iPr_3)_2$ is likely to involve one of the NH_2 protons (eqn. (7)).



Q

(7)

This may be the lowest energy path because it does *not* require a divalent $M^{II}H(H_2)$ intermediate (especially costly for a 5d metal), and because that d^6 intermediate might bind H_2 especially strongly. In *addition*, there is abundant evidence[37–39] for hydrogen bonding between a hydride ligand and a nearby acidic proton, so H^a and H^b in **Q** may already have some bonded character. Concrete evidence for this is the observed higher barrier for scrambling *one* hydride with the other two in $OsH_3(OC_6H_4NH_2)(P^iPr_3)_2$ *vs.* the Ru analog. The more electropositive character of a 5d metal (*vs.* 4d) should make hydride on Os more Brønsted basic, hence forming a stronger hydrogen bond.

(5) For osmium only, we have studied *ortho*-phenylenediamine reagents for their potential to introduce an *ortho*-diamido chelate. Here, a second mole of diamine was anticipated to serve the role of base, perhaps making a deprotonated (lithium) amide unnecessary. This reaction proceeds satisfactorily for *ortho*-phenylenediamine and its ring methyl derivative, with loss of *two* amine protons, to give the dihydride of Os^{IV}. That is, H_2 is released during the reaction to give an Os^{IV} diamide.

(6) When one *ortho*-phenylenediamine nitrogen carries one methyl group, this secondary amine center changes the reaction progress considerably. Although an adduct is formed between $Os(H)_3Cl(P^iPr_3)_2$ and $NHMe(C_6H_4)NH_2$, there is no further reaction in the presence of additional (free) $NHMe(C_6H_4)NH_2$. The adduct persists, with no loss of H_2 or HCl. The addition of $^tBuHC{=}CH_2$, as a hydrogen acceptor, delivers $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$, together with amine hydrochloride and hydrogenated olefin. Steric factors at the secondary amine center may be the source of the trouble, until a lower coordination number can be achieved by olefin hydrogenation.

(7) The molecule $Os(H)_2(NMeC_6H_6NH)(P^iPr_3)_2$ is unique among all those 6 coordinate species studied here in showing *inequivalent* hydrides (but still time average equivalent phosphorus nuclei). This is attributed to steric conflicts between the NMe group and a P^iPr_3 group in the transition state for equivalencing the hydrides, which is deduced to involve a planar P_2OsN_2 substructure.

(8) The mechanism of the ligand exchange reaction of $Os(H)_2(NMeC_6H_4NH)(P^iPr_3)_2$ with catechol involves proton transfer, and that catechol proton goes to Os, not N, indicating that each amide lone pair is strongly involved in bonding to its attached π-acids, Os^{IV} and the aryl π* orbital.

(9) With regard to the question of intramolecular redox between **M** and **N**, the fact that the quinoid structure involves divalent metal leads to some predictions. First, this should adopt an octahedral structure, which is not observed in the two structures reported here. In addition, such an octahedral structure is less likely to be fluxional, given the general rigidity that characterizes d^6, octahedral molecules. Taken together, the structures and fluxionality observed here establish a picture of the d^4, six-coordinate potential energy surface as having low barriers between nearly degenerate alternative structures. Not even catecholate ligand, a weak π-donor, brings the $RuH_2(P^iPr_3)_2$ moiety to oxidation state II.

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