Reactivity patterns of the unsaturated Os(0) species $Os(NO)(CO)(PBu^t_2Me)_2^+$†

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$OsHCl(CO)L_2$ (L = PBu^t_2Me) is transformed to $OsCl(NO)(CO)L_2$ by *p*-$MeC_6H_4SO_2N(NO)Me$. Chloride removal with $NaBAr'_4$ [Ar′ = 3,5-$(CF_3)_2C_6H_3$] yields the nonplanar, unsaturated Os(0) compound $[Os(NO)(CO)L_2]BAr'_4$, which is shown to be more reactive towards oxidative addition than its Ru analog. It adds H_2, and the resulting $Os(H)_2(NO)(CO)L_2^+$ shows broad coalesced hydride NMR signals at 25 °C but inequivalent sites (^{1}H NMR spectra) at −32 °C. This cation is deprotonated by NEt_3 to give trigonal bipyramidal $OsH(NO)(CO)L_2$. The cation $Os(NO)(CO)L_2^+$ adds CO. Reaction of $Os(NO)(CO)L_2^+$ with PhC_2H gives first a 1 : 1 adduct, then the oxidative addition product $OsH(C_2Ph)(NO)(CO)L_2^+$, then the vinylidene complex $Os(CCHPh)(NO)(CO)L_2^+$; a mixture of these cations can be deprotonated by NEt_3 to give $Os(CCPh)(CO)(NO)L_2$. Reaction of $Os(NO)(CO)L_2^+$ with $Me_3SiC{\equiv}CSiMe_3$ gives $Os[CC(SiMe_3)_2](NO)(CO)L_2^+$, which can be doubly hydrolyzed to give $Os(CCH_2)(NO)(CO)L_2^+$. HCCH forms an η^2-HCCH adduct, which does not isomerize to $Os(CCH_2)(CO)(NO)L_2^+$ even at 60 °C.

We have reported our systematic investigation of the existence of an isolable 16-electron Ru(0) complex, $Ru(CO)_2L_2$ (L = PBu^t_2Me).[1] This metastability (persistence) contrasts to all other zerovalent ruthenium species devoid of *π-donor* ligands [this thus excludes $Ru(NO)ClL_2$], which are short-lived transients. Our study of $Ru(CO)_2L_2$ showed its remarkable nonplanar structure to originate from a high degree of back donation to the two CO ligands, and also revealed its high reactivity as a *π-donor* (and reducing agent), with only weak σ-Lewis acidity: it does not bind pyridine, MeCN or N_2.

A 19 kcal mol^{-1} barrier to inversion of nonplanar Ru(0), *via* a planar structure, was subsequently measured[2] on $Ru(NO)(CO)L_2^+$. This study revealed that $Ru(NO)(CO)L_2^+$ is less reactive than isoelectronic $Ru(CO)_2L_2$ in all reactions that involve transfer of electron density from the metal to the reagent. This is a predictable consequence of replacement of one CO of $Ru(CO)_2L_2$ by the stronger π-acid NO^+.

We report here the results of changing the metal with the synthesis and properties of $Os(NO)(CO)L_2^+$. The one predictable consequence of the Ru → Os change is that the metal is more electron-rich, more Brønsted-basic, and more oxidizable. In this study, we have concentrated on those reactions that *failed* for $Ru(NO)(CO)L_2^+$, but which have been characterized for $Ru(CO)_2L_2$. In this way, we hoped to use those reagents that are most discriminating, or diagnostic of differences in reactivity between $Ru(NO)(CO)L_2^+$ and $Os(NO)(CO)L_2^+$. This study also furnishes an opportunity to better understand the alkyne-to-vinylidene isomerization.[3]

Experimental

All manipulations were done under an atmosphere of dry, O_2-free Ar employing a Vacuum Atmospheres inert atmosphere glovebox or standard Schlenk-line techniques. The solvents were reagent grade and distilled from the appropriate drying agents under Ar. Phenylacetylene was purchased from Aldrich and distilled before use. Bis(trimethylsilyl)acetylene was purchased from PCR and was freeze-pump-thaw degassed before use. Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulphonamide) was purchased from Aldrich and stored at 5 °C and used without further purification. H_2 and CO were purchased from Air Products. D_2 was purchased from Spectra Products in 99% purity. All gases were used without further purification and were measured using a calibrated gas manifold. The ^{1}H, ^{13}C and ^{31}P NMR were collected on a Varian Gemini 2000 or Inova 400 (^{1}H: 300, 400 MHz; ^{13}C: 100 MHz; ^{31}P: 122, 162 MHz). ^{1}H NMR were referenced to residual solvent peaks as internal standards. ^{31}P NMR were referenced to an external standard of 85% H_3PO_4. Infrared data were collected on a Nicolet 510P FT-IR.

Synthesis and reactivity

$OsCl(CO)(NO)(PBu^t_2Me)_2$. A suspension of $OsHCl(CO)(PBu^t_2Me)_2$ (501.4 mg, 0.872 mmol) and diazald (301.8 mg, 1.409 mmol) in 20 mL ethanol was stirred for 3 h at 20 °C. The solution color changed from orange to brown. Raising the temperature to boiling caused all the solid to dissolve. Slow cooling then produced small brown crystals. These were washed with ethanol and dried under vacuum to give 348 mg (0.576 mmol, 66%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.63 (vt, 6H, PCH_3, J_{PH} = 2.7 Hz); 1.29 (vt, 18H, $PCCH_3$, J_{PH} = 5.1 Hz); 1.24 (vt, 18H, $PCCH_3$, J_{PH} = 5.1 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 22.65 (s). IR (CD_2Cl_2): ν(CO) = 1898, ν(NO) = 1539 cm^{-1}.

$[Os(CO)(NO)(PBu^t_2Me)_2]BAr'_4$ [Ar′ = 3,5-$(CF_3)_2C_6H_3$]. To a solution of $OsCl(CO)(NO)(PBu^t_2Me)_2$ (134.3 mg, 0.22 mmol) in 35 mL CH_2Cl_2 was added $NaBAr'_4$ (214.0 mg, 1.09 equiv). With 30 min of stirring at room temperature, the color of the solution became a deep red. Concentration of the solution and cooling to −40 °C for 3 days caused the formation of deep red crystals. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.75 (s, 8H, *o*-Ar*H*); 7.58 (s, 4H, *p*-Ar*H*); 1.92 (vt, 6H, PCH_3, J_{PH} = 3.3 Hz); 1.37 (vt, 18H, $PCCH_3$, J_{PH} = 7.8 Hz); 1.28 (vt, 18H, $PCCH_3$, J_{PH} = 7.8 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 44.70 (s). IR (CD_2Cl_2): ν(CO) = 1952, ν(NO) = 1705 cm^{-1}. Anal. calcd for $OsC_{51}H_{54}BNO_2F_{24}P_2$ (found): C 42.78 (43.23); H 3.80 (3.57).

† *Non-SI units employed*: 1 kcal = 4.184 kJ; 1 torr ≈ 133 Pa.

[Os(H)$_2$(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (86.8 mg, 0.061 mmol) in 20 mL CH_2Cl_2 in a 50-mL flask was added excess H_2 (700 torr, 32 equiv). The color of the solution changed from deep red to faint yellow within the time of mixing. Slow cooling to −40 °C caused the formation of pale peach crystals. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.88 (s, 8H, *o*-Ar*H*); 7.78 (s, 4H, *p*-Ar*H*); 1.90 (vt, 6H, PC*H*$_3$, J_{PH} = 3.9 Hz); 1.36 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.6 Hz); 1.35 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.6 Hz); − 5.4 (br s, 2H, Os*H*); ^{1}H NMR (CD_2Cl_2, −40 °C): δ − 4.37 (t, 1H, Os*H*, J_{PH} = 17.4 Hz); −6.85 (t, 1H, Os*H*, J_{PH} = 20.7 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 34.88 (s). IR (CD_2Cl_2): ν(CO) and (OsH) = 2099, 2067, 1820; ν(NO) = 1794 cm^{-1}. Anal. calcd for $OsC_{51}H_{56}BNO_2F_{24}P_2$ (found): C 42.71 (42.40); H 3.94 (3.53).

OsH(CO)(NO)(PBu$^t_2$Me)$_2$. The complex [Os(H)$_2$(CO)-(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (13.8 mg, 0.0096 mmol) in 500 μL CD_2Cl_2 was deprotonated in an NMR tube with NEt_3 (1.25 μL, 1.01 equiv) within the time of mixing to form an orange-brown solution. ^{1}H NMR (CD_2Cl_2, 20 °C): 1.72 (vt, 6H, PC*H*$_3$, J_{PH} = 3.3 Hz); 1.304 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.0 Hz); 1.298 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.0 Hz); − 6.17 (t, 1H, Os*H*, J_{PH} = 24 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 36.3 (s). IR (CD_2Cl_2): ν(CO) = 1882, ν(NO) = 1609 cm^{-1}.

[Os(D)$_2$(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. A freeze-pump-thawed NMR solution of [Os(H)$_2$(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (13.7 mg, 0.0096 mmol) in 500 μL CD_2Cl_2 was reacted with 270 torr (4.6 equiv) D_2 at 25 °C. Within 20 min of vigorous mixing, equilibrium had been reached (as observed by ^{1}H NMR over a period of 24 h) to form [Os(D)$_2$(CO)-(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ + H_2. All other spectroscopic features were identical with the all protio version except IR: IR (CD_2Cl_2): ν(CO) = 2058, ν(NO) = 1809 cm^{-1}.

[Os(HCCH)(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To a degassed solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (31.7 mg, 0.022 mmol) in 600 μL CD_2Cl_2 was added 700 torr (4.4 equiv) C_2H_2. Upon mixing, the solution turned yellow and the excess acetylene was removed *via* vacuum. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 8.19 (s, 1H, *H*CC); 7.73 (s, 8H, *o*-Ar*H*); 7.57 (s, 4H, *p*-Ar*H*); 5.97 (s, 1H, *H*CC); 1.32 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.6 Hz); 1.30 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.6 Hz); 0.92 (vt, 6H, PC*H*$_3$, J_{PH} = 4 Hz). ^{13}C NMR (CD_2Cl_2, 20 °C): 188.1, (t, *C*O, J_{PC} = 5 Hz); 162.3, (q, B*C*, J_{BC} = 50.7 Hz); 135.4, 130.0, 129.6, 129.3, 129.2, 129.0, 126.6, 123.9, 121.2, 118.1, (BAr); 101.1, (s, *C*C); 77.6, (s, C*C*); 34.3, (vt, P*C*CH$_3$, J_{PC} = 10 Hz); 33.7, (vt, P*C*CH$_3$, J_{PC} = 10 Hz); 29.7, (s, PC*C*H$_3$); 29.5, (s, PC*C*H$_3$); 6.1, (vt, P*C*H$_3$, J_{PC} = 20 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 16.3 (s). IR (CD_2Cl_2): ν(CO) = 2014, ν(NO) = 1727 cm^{-1}.

[Os{CC(SiMe$_3$)$_2$}(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To a cooled (−20 °C) solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (16.5 mg, 0.011 mmol) in 500 μL CD_2Cl_2 was added excess bis(trimethylsilyl)acetylene (5 μL, 0.022 mmol). Upon rapid inversion of the tube, the solution color changed from red-brown to golden yellow; ^{31}P and ^{1}H NMR showed conversion to one product. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.7 (s, 8H, *o*-Ar*H*); 7.6 (s, 4H, *p*-Ar*H*); 1.8 (vt, 6H, PC*H*$_3$, J_{PH} = 3 Hz); 1.35 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.7 Hz); 1.32 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.3 Hz); 0.35 (s, 9H, SiC*H*$_3$); 0.27 (s, 9H, SiC*H*$_3$). ^{13}C NMR (CD_2Cl_2, −20 °C): δ 273.6 (α-*C*C, J_{PC} = 11.7 Hz); 184.8 (t, *C*O, J_{PC} = 7.6 Hz); 162.0 (quartet, B*C*, J_{BC} = 50 Hz); 135.0, 129.5, 129.2, 128.9, 128.6, 126.2, 123.4, 120.7, 117.8 (BAr); 113.5 (s, β-C*C*); 40.2 (vt, P*C*CH$_3$, J_{PC} = 11.0 Hz); 39.6 (vt, P*C*CH$_3$, J_{PC} = 11.0 Hz); 29.9 (s, PC*C*H$_3$); 29.7 (s, PC*C*H$_3$); 8.4 (vt, P*C*H$_3$, J_{PC} = 15.5 Hz); 2.8 (s, Si*C*H$_3$). ^{31}P NMR (CD_2Cl_2, − 20 °C): δ 11.6 (s).

[Os(CCH$_2$)(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. Bis(trimethylsilyl)acetylene (10 μL, 0.044 mmol) was added to a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (28.7 mg, 0.020 mmol) in 500 μL CD_2Cl_2. Water (0.2 μL, 0.011 mmol) was then added *via* syringe to this solution. Two new species were seen by ^{31}P and ^{1}H NMR. [Os(CCH$_2$)(CO)- (NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ has the following characteristic ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.71, 7.55 (12H, BAr$'_4$); 3.34 (t, 2H, CCH$_2$, J_{PH} = 6.0 Hz); 1.80 (vt, 6H, PMe, J_{PH} = 3.6 Hz); 1.35, 1.30 (2 vt, 18H, PBu^t, J_{PH} = 7.4 Hz). ^{31}P NMR (CD_2Cl_2, 293 K): δ 17.47 s. [Os{CCH(SiMe$_3$)}(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ has the following characteristic ^{1}H NMR (CD_2Cl_2, 293 K): δ 7.71, 7.55 (12H, BAr$'_4$); 3.70 (t, 1H, CCH, J_{PH} = 6.0 Hz); 1.77 (vt, 6H, PMe, J_{PH} = 3.2 Hz); 0.23 (s, 9H, SiMe$_3$). ^{31}P NMR (CD_2Cl_2, 293 K): δ 15.88 s.

[Os(CO)$_2$(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To an NMR tube containing a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (12.0 mg, 0.0084 mmol) in 600 μL CD_2Cl_2 was added CO (400 torr, 7.6 equiv). Upon mixing, the solution turned a very pale peach color. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.75 (s, 8H, *o*-Ar*H*); 7.58 (s, 4H, *p*-Ar*H*); 1.92 (vt, 6H, PC*H*$_3$, J_{PH} = 4.5 Hz); 1.37 (vt, 36H, PCC*H*$_3$, J_{PH} = 10.5 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 20.8 (s). IR (CD_2Cl_2): ν(CO) = 2039, 1981; ν(NO) = 1723 cm^{-1}. Anal. calcd for $OsC_{52}H_{54}BNO_3F_{24}P_2$ (found): C 42.78 (42.52); H: 3.72 (3.51).

[Os(η^2-HC≡CPh)(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ in 500 μL CD_2Cl_2 (15.9 mg, 0.011 mmol) was added 1.20 μL (0.011 mmol) of phenylacetylene. Upon removing the NMR tube from the glovebox, the sample was immediately cooled. ^{31}P NMR showed the predominant first product of the reaction to be the η^2-bonded alkyne. ^{1}H NMR (CD_2Cl_2, 5 °C): δ 8.1 (s, 1H, HCCPh); 7.72 (s, 8H, *o*-BAr*H*); 7.56 (s, 4H, *p*-BAr*H*); 7.52, 7.45, 7.39 (selected C_6H_5 peaks); 1.32 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); 1.31 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); 0.82 (vt, 6H, PC*H*$_3$, J_{PH} = 3.9 Hz). ^{31}P NMR (CD_2Cl_2, 5 °C): δ 22.5 (s).

[OsH(C≡CPh)(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. This compound is also evident in the above reaction. At the earliest observation time, the hydrido alkynyl was present in approximately 5% abundance. With time evolution, this product never gained in mole fraction. It was identified by the following spectroscopic signals. ^{1}H NMR (CD_2Cl_2, 5 °C): δ 1.99 (vt, 6H, PC*H*$_3$, J_{PH} = 3.9 Hz); 1.48 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); 1.44 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); − 2.03 (t, 1H, OsH, J_{PH} = 7.2 Hz). ^{31}P NMR (CD_2Cl_2, 5 °C): δ 25.1 (s).

[Os{C≡C(H)Ph}(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$. To a 100-mL flask containing a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr$'_4$ (74.4 mg, 0.052 mmol) in 50 mL CH_2Cl_2 was added 6.4 μL (1.12 equiv) PhCCH. Over 1.5 h of stirring at room temperature, the solution changed from pale peach (η^2-alkyne) to deep red. The solution was filtered through Celite. The solvent was then removed in vacuum to yield a red-brown solid. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.73 (t, 8H, *o*-BAr*H*, J_{PH} = 2.3 Hz); 7.57 (s, 4H, *p*-BArH); 7.35 (t, 2H, *m*-Ph, J_{HH} = 7.8 Hz); 7.26 (br t, 1H, *p*-Ph, J_{HH} = 7.8 Hz); 7.01 (d, 2H, *o*-Ph, J_{HH} = 7.5 Hz); 4.82 (t, 1H, C*H*(Ph), J_{PH} = 6.3 Hz); 1.68 (vt, 6H, PC*H*$_3$, J_{PH} = 3.6 Hz); 1.40 (vt, 18H, PCC*H*$_3$, J_{PH} = 8.4 Hz); 1.34 (vt, 18H, PCC*H*$_3$, J_{PH} = 8.4 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 23.0 (br s). ^{13}C NMR (CD_2Cl_2, 20 °C): δ 316.7 (t, α-*C*C, J_{PC} = 17 Hz); 182.4, (t, *C*O, J_{PC} = 5 Hz); 162.6, (quartet, BC, J_{BC} = 50.9 Hz); 135.6, 130.8, 130.3, 129.9, 129.4, 129.0, 128.6, 127.4, 127.2, 123.5, 119.9, 118.2 (BAr, Ph); 126.5 (t, β-C*C*, J_{PC} = 4.8 Hz); 40.3, 40.1 (PC*C*H$_3$); 29.5 (PC*C*H$_3$); 7.2 (P*C*H$_3$). IR (CD_2Cl_2): ν(CO) = 2019, ν(NO) = 1730 cm^{-1}.

Os(C≡CPh)(CO)(NO)(PBu$^t_2$Me)$_2$. Method (a). To a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr′$_4$ (12.2 mg, 0.0085 mmol) in 500 μL CD_2Cl_2 was added 0.95 μL (1.02 equiv) of phenylacetylene. With all isomers [OsH(C≡CPh)(CO)(NO)(PBu$^t_2$Me)$_2$$^+$, Os{C≡C(H)Ph}(CO)(NO)(PBu$^t_2$Me)$_2$$^+$, Os(η^2-HC≡CPh)(CO)(NO)(PBu$^t_2$Me)$_2$$^+$] present, 3.0 μL (2.5 equiv) of NEt_3 was added *via* syringe. Immediately the solution turned golden yellow. The CD_2Cl_2 was pumped away and the solid was extracted with three 1-mL portions of pentane; the pentane was removed *via* vacuum to yield a yellow solid.

Method (b). An independent synthesis of this compound was achieved by adding LiCCPh (38.8 mg, 0.359 mmol) to a toluene solution of OsCl(CO)(NO)(PBu$^t_2$Me)$_2$ and stirring for 12 h. Removal of toluene and extraction of the resultant material with benzene produced the above product in greater than 95% purity. The complex was identified by the following spectroscopic properties. ^{1}H NMR (C_6D_6, 20 °C): δ 7.35 (d, 2H, *m*-Ph, J_{HH} = 7.8 Hz); 7.26 (br t, 1H, *p*-Ph, J_{HH} = 7.8 Hz); 7.01 (d, 2H, *o*-Ph, J_{HH} = 7.5 Hz); 1.39 (vt, 6H, PC*H*$_3$, J_{PH} = 3.6 Hz); 0.95 (vt, 18H, PCC*H*$_3$, J_{PH} = 6.9 Hz); 0.83 (vt, 18H, PCC*H*$_3$, J_{PH} = 6.6 Hz). ^{13}C NMR (C_6D_6, 20 °C): δ 188.7 (t, *C*O, J_{PC} = 7.2 Hz); 130.9, 130.4, 125.4 (Ph); 126.9 (t, α-*C*CPh, J_{PC} = 11.9 Hz); 106.3 (t, β-C*C*Ph, J_{PC} = 16.7 Hz); 30.3 (s, PCC*H*$_3$); 30.0 (s, PC*C*H$_3$); 8.7 (t, P*C*H$_3$, J_{PC} = 16.4 Hz). ^{31}P NMR (C_6D_6, 20 °C): δ 16.6 (s). IR (CD_2Cl_2): ν(CO) = 1902, ν(NO) = 1620, ν(C≡C) = 2085 cm^{-1}.

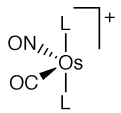
[Os{C≡C(H)(Bu^t)}(CO)(NO)(PBu$^t_2$Me)$_2$]BAr′$_4$. To a solution of [Os(CO)(NO)(PBu$^t_2$Me)$_2$]BAr′$_4$ (17.8 mg, 0.0124 mmol) in 500 μL CD_2Cl_2 was added 2 μL (3.306 equiv) *tert*-butylacetylene. There was no noticeable color change. After 0.5 h at room temperature, ^{1}H and ^{31}P NMR showed, through analogy with other complexes, that only the vinylidene was present. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 7.73 (t, 8H, *o*-BAr*H*, J_{PH} = 2.1 Hz); 7.57 (s, 4H, *p*-BArH); 3.76 (t, 1H, C*H*(Bu^t), J_{PH} = 6.0 Hz); 1.80 (vt, 6H, PC*H*$_3$, J_{PH} = 3.9 Hz); 1.38 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); 1.34 (vt, 18H, PCC*H*$_3$, J_{PH} = 7.2 Hz); 1.11 (s, 9H, CC[C(C*H*$_3$)$_3$]). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 17.6 (s).

Results

Synthesis and characterization of OsCl(NO)(CO)L$_2$ and Os(NO)(CO)L$_2$$^+$

Reaction of OsHCl(CO)L$_2$ with diazald at reflux in ethanol yields OsCl(NO)(CO)L$_2$.[4] The ^{1}H NMR spectrum of the equivalent P–Me groups (a virtual triplet) is consistent with *trans* phosphines and the diastereotopic Bu^t protons are consistent with the OsCl(NO)(CO) unit being coplanar. While this is equally consistent with a trigonal-bipyramidal structure with a linear OsNO unit, the ν(CO) (1898 cm^{-1}) and ν(NO) (1539 cm^{-1}) frequencies are sufficiently similar to those of the crystallographically characterized RuX(NO)(CO)L$_2$[2] that we assign the osmium complex a square-pyramidal structure with bent NO.

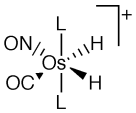
Chloride is efficiently abstracted from OsCl(NO)(CO)L$_2$ by NaBAr′$_4$ [5] (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) at 25 °C in CH_2Cl_2 to give four-coordinate [Os(NO)(CO)L$_2$]BAr′$_4$. The diasteroeotopic Bu^t ligands require a nonplanar OsNCP$_2$ unit (and rule out either a planar geometry or a rapid inversion at Os) and thus indicate structure **1**, analogous to that of the Ru species. This geometry, derived from a trigonal bipyramid by removal of one equatorial ligand, is clearly "prepared" for ligand addition. The ν(NO) value (1705 cm^{-1}) of Os(NO)(CO)L$_2$$^+$ is too high for a bent OsNO unit, and is close to that of the Ru analog (1709 cm^{-1}). The ν(CO) value, 1952 cm^{-1}, is considerably higher than that of OsCl(NO)(CO)L$_2$. The rise of ν(NO) upon chloride removal, 166 cm^{-1}, is strong evidence for conversion from a bent to a linear NO.



1

Reactivity of Os(NO)(CO)L$_2$$^+$

H$_2$. This unsaturated Os(0) cation reacts with H_2 at 25 °C in CD_2Cl_2 to give Os(H)$_2$(NO)(CO)L$_2$$^+$. The ruthenium analog of **1** shows no reaction at −80 °C in CD_2Cl_2 under 1 atm H_2. The osmium cation shows (^{1}H NMR) a broad, unstructured hydride signal at room temperature, together with diastereotopically inequivalent Bu^t signals. By −32 °C, the hydride region has decoalesced into two signals, whose average chemical shift is within 1.2 ppm of the 25 °C value. The chemical shift of the ^{31}P{^{1}H} NMR singlet is essentially unchanged within 0.3 ppm between −70 and +25 °C. These results are all consistent with a species of structure **2**, with no significant (*i.e.*, >5%) loss of H_2 at the temperatures studied. The infrared spectrum of Os(H)$_2$(NO)(CO)L$_2$$^+$ shows ν(NO) at 1794 cm^{-1}, but three bands at 2067, 2099, and 1820 cm^{-1} for Os–H and CO modes. The value of ν(CO), 2058 cm^{-1}, is better derived from Os(D)$_2$(NO)(CO)L$_2$$^+$, which shows ν(NO) at 1809 cm^{-1}. This is the highest ν(CO) value observed in this study, a result of reduced π-donation by Os(II) and of being *trans* to a hydride ligand. The IR spectrum of Os(D)$_2$(NO)(CO)L$_2$$^+$ after exposure to vacuum at 25 °C shows no Os(NO)(CO)L$_2$$^+$, indicating that loss of dihydrogen is not facile; oxidative addition is "complete". The ^{1}H NMR hydride signal becomes a triplet at 80 °C in $(CDCl_2)_2$, showing that the fluxionality is intramolecular.



2

A solution of Os(H)$_2$(NO)(CO)L$_2$$^+$ in CD_2Cl_2 was treated with 270 torr (~4.6 equiv) D_2 at 25 °C. Within 20 min of vigorous mixing, equilibrium had been reached (subsequently observed by ^{1}H NMR for 24 h) to form Os(D)$_2$(NO)(CO)L$_2$$^+$ and H_2. The facility of this exchange reaction is surprising. It is interesting that trace amounts of HD were produced and detected during the exchange of H_2 for D_2. The mechanistic conclusions that might be drawn from this observation are one of the following: nitrosyl bends from linear, CO dissociates, or phosphine dissociates.

Deprotonation of Os(H)$_2$(NO)(CO)L$_2$$^+$ with NEt_3 yields OsH(NO)(CO)L$_2$. The Bu^t protons show diastereotopic inequivalence by ^{1}H NMR at 25 °C. A hydride triplet and ^{31}P{^{1}H} NMR singlet are consistent with an intact, mirror-symmetric, five-coordinate structure at 25 °C. The similarity of the ν(NO) and ν(CO) values to those of crystallographically characterized RuH(NO)(CO)L$_2$ supports the assignment of a trigonal bipyramid with axial phosphines and equatorial hydride, NO and CO.

CO. Os(NO)(CO)$_2$L$_2$$^+$ is formed immediately on addition of CO. The ν(NO) value rises from 1705 to 1723 cm^{-1} on addition of CO. The Bu^t protons are now equivalent in this molecule.

Acetylenes. (*a*) *PhCCH*. [Os(CO)(NO)(PBu$^t_2$Me)$_2$]$^+$ reacts with < 1 equiv phenylacetylene in CD_2Cl_2. At −55 °C, the first product (Fig. 1) is an η^2-bound species (**A**, Scheme 1). The acetylene proton appears at 8.9 ppm as a singlet. With warming to −25 °C, a hydride product **C** appears at −2.03

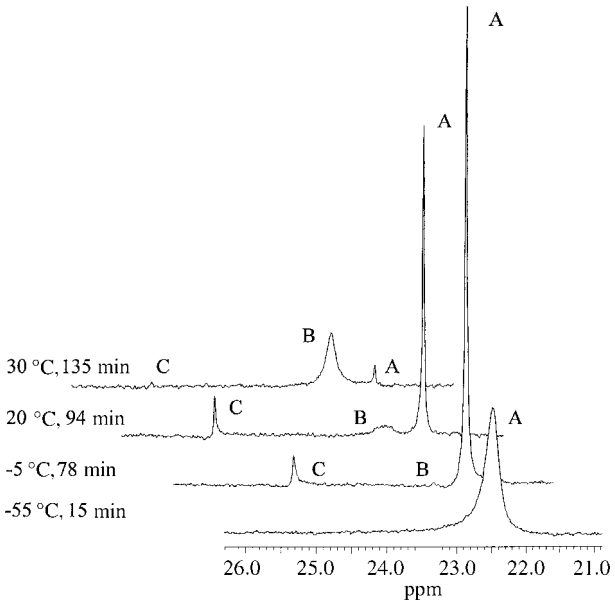
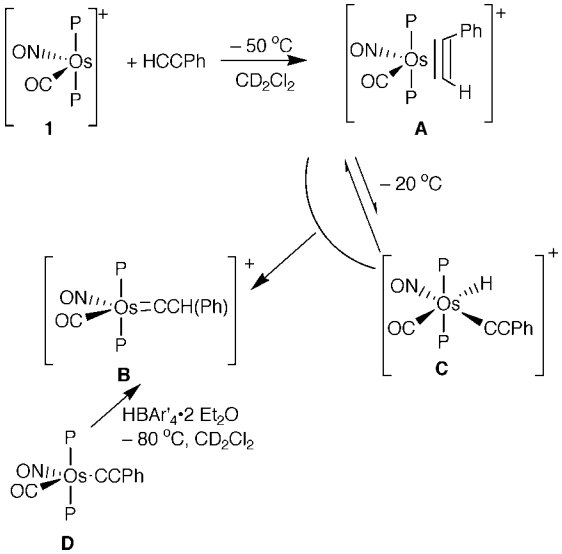


Fig. 1 Kinetic evolution of the 162 MHz $^{31}P\{^1H\}$ NMR spectrum of the reaction of $Os(NO)(CO)L_2^+$ with PhCCH in CD_2Cl_2 as the temperature (in °C) is increased. (*A*) $Os(NO)(CO)(\eta^2\text{-}HC_2Ph)L_2^+$, (*B*) $Os(NO)(CO)[CC(H)(Ph)]L_2^+$, (*C*) $Os(NO)(CO)H(CCPh)L_2^+$.

ppm (triplet). Throughout the rest of the reaction, this hydrido acetylide and the η^2-acetylene species remain in the same mole ratio, which suggest that they are in equilibrium. After being at room temperature for 10 min (Fig. 1), the initial formation of a third, thermodynamic product was seen. This last product, the vinylidene isomer (**B**, Scheme 1), displayed a proton NMR signal at 4.8 ppm as a triplet due to proton–phosphorus coupling. After 1.5 h at 30 °C, nearly all η^2-acetylene and hydrido acetylide had been converted into vinylidene (Fig. 1).

We tested whether this isomerization could be acid-base catalyzed. A similar reaction was carried out in CD_2Cl_2 with added trace amounts of NEt_3 or H_2O. Upon adding alkyne, then trace NEt_3, deprotonation occurs, to form trace $Os(CCPh)(CO)(NO)(PBu^t_2Me)_2$, **D**. After 5 h isomerization to vinylidene was complete although the uncharged acetylide **D** complex still remained. In the presence of added water, no new species were seen (*i.e.*, no water adducts) and the isomerization to vinylidene appeared to proceed on the same time scale as the control ("dry") reaction. If the reaction was run in the presence of trace $[H(OEt_2)_2]BAr'_4$, a strong acid, it



Scheme 1

reached completion in 2.5 h; therefore no significant inhibition by acid *or* base was detected. We believe that these three conditions sufficiently test for an acid-base pathway and we conclude that the isomerization must be intramolecular (a 1,2- or 1,3-shift) or bimolecular.[6]

It was interesting to note that NEt_3 deprotonates these species. In certain of these reactions, the proton was removed from either the hydrido acetylide or the η^2-acetylene, since they were the only species in solution when the base was added. But, in a separate experiment where all three species were in solution and >1 equiv. NEt_3 was added, all species were deprotonated. This indicates that either all species are acidic or that there is an equilibrium between the acidic species and the other two species.

We have attempted to enter the manifold of compounds in Scheme 1 from another point, **D**. Protonation of $Os(CCPh)(CO)(NO)(PBu^t_2Me)_2$ with $[H(OEt_2)_2]BAr'_4$ in CD_2Cl_2 at −80 °C gives (^1H and ^{31}P NMR evidence) only the product of protonation of C_β: the cationic vinylidene complex, **B**. Raising the temperature of this solution progressively to 20 °C produces no new species. This permits the conclusion that protonation does not occur at Os but only at the β-carbon of the acetylide; it is also consistent with the vinylidene complex as the most thermodynamically stable species in Scheme 1.

(*b*) *HCCH*. $[Os(CO)(NO)(PBu^t_2Me)_2]BAr'_4$ reacts with excess C_2H_2 in CD_2Cl_2 with a color change to light yellow to give a 1:1 adduct. The ν(CO) and ν(NO) values of this product are considerably higher than those of $Os(NO)(CO)L_2^+$, indicating that HCCH behaves more as a π-acid than as a donor. Excess acetylene was then removed in vacuum, but this molecule shows no tendency to transform to a hydrido acetylide or to a vinylidene species, even after heating to 60 °C for 30 min in $C_2D_2Cl_4$. The cation is stereochemically rigid at 25 °C in both ^1H and ^{13}C NMR: two acetylene hydrogen and carbon chemical shifts are seen. The ^{13}C chemical shift values, 101.0 and 77.6 ppm, are consistent[7] with the acetylene functioning as a 2-electron donor to Os. ^1H NMR spectra at 60 °C in $C_2D_2Cl_4$ show broadening of the 5.9 and 8.1 ppm acetylene signals, while the $^{31}P\{^1H\}$ NMR signal remains sharp at this temperature. Therefore, the process beginning at this temperature must be rotation of acetylene, not acetylene loss. Raising the temperature further caused degradation of the acetylene complex.

(*c*) *$Me_3SiCCSiMe_3$*. Bis(trimethylsilyl)acetylene reacted with $[Os(CO)(NO)(PBu^t_2Me)_2]^+$; the only product observed already at −20 °C is the vinylidene $[Os(CC(SiMe_3)_2)(CO)(NO)(PBu^t_2Me)_2]^+$, best characterized by a ^{13}C NMR signal at 274 ppm for C_α. The rapid isomerization of bis(trimethylsilyl)acetylene to its vinylidene is not unprecedented.[3q] Its speed relative to the other isomerizations indicates that trimethylsilyl facilitates the movement of groups either by electronically stabilizing the transition state (1,2- or 1,3-isomerizations) or by raising the ground state of the η^2-bound alkyne by greater steric hindrance.

Si–C bond hydrolysis. The addition of water to the bis(trimethylsilyl)vinylidene species, or even adventitious water or nucleophile, produced two new species. They were identified by two new triplets in the vinylidene region of the ^1H NMR and two new singlets in the ^{31}P NMR. Hydrolysis of $SiMe_3$ groups is a common occurrence for TMS groups connected to the β-carbon of a vinylidene.[3q,8] Using a ^{13}C NMR driven equilibrium polarization transfer experiment we were able to identify the final product as $[Os(CCH_2)(CO)(NO)L_2]^+$. We presume the other species to be the product of a single hydrolysis, $[Os\{CCH(SiMe_3)\}(CO)(NO)L_2]^+$. Both products were also formed when $HCCSiMe_3$ was added to $[Os(CO)(NO)L_2]^+$. The observed adventitious Si–C bond cleavage is also proof that, in solutions of these cationic complexes, there is otherwise unrecognized nucleophile present. This has clear implica-

tions for understanding the mechanism of the proton migration isomerizations between M(HCCR), HMCCR and MCCHR.

(*d*) *Bu^{t}CCH*. In order to better understand the importance of steric and electronic factors in the isomerization process, we reacted **1** with *tert*-butylacetylene at room temperature. This resulted in formation of the vinylidene species by the time of the first observation (30 min) in ^{1}H NMR. A triplet at 3.76 ppm is characteristic of the vinylidene complex. The reaction was repeated at low temperature (−70 °C). At the time of the first observation (≈3 min), three new species were seen by ^{31}P NMR. None of the three species was the previously seen vinylidene. The most abundant species was established to be a hydrido alkynyl species, with a hydride signal at −2.3 ppm in the ^{1}H NMR. We presume the other two species to be two isomers of the η^2-alkyne species, differing by location of the Bu^t group. Warming the solution by 10 °C increments shows that by −40 °C, nearly all species had transformed into the hydrido alkynyl complex. With further warming to −20 °C, one observes the initial conversion to a vinylidene product. Complete conversion from the hydrido alkynyl to the vinylidene was accomplished within 15 min at room temperature. Thus, compared to phenylacetylene, conversion to hydrido alkynyl and vinylidene isomers occurs at lower temperatures for Bu^{t}CCH.

Discussion

There have been many examples of isomerization of terminal acetylenes to vinylidene on Group VIII metals (primarily Ru).[3,9] Most transformations have occurred on a M^{II} species and are often suggested to proceed *via* a 1,2-hydrogen shift of the η^2-bound alkyne, presumably because oxidative addition at a M^{II} center leading from d^6 to d^4 is too hard to achieve. Recently, a 1,3-isomerization for Ru involving a formally Ru^{IV} species, [Cp*RuH(C≡CR)(dippe)][BPh$_4$], was reported.[3e] That work was generally accomplished in MeOH solvent, where an acid/base mechanism cannot be excluded; in particular, Brønsted acidity by a proton on the metal or on an acetylene carbon should be enhanced by the cationic character of such intermediates. We report here on a cationic Os^o, d^8 complex carrying two π-accepting ligands, CO and NO. Although the hydrido cation species, [Os(H)$_2$(CO)(NO)L$_2$]$^+$ and [OsH(CCPh)(CO)(NO)L$_2$]$^+$, can be deprotonated by NEt$_3$, we have found no evidence to suggest that the isomerization of η^2 alkyne or hydrido acetylide to vinylidene was catalyzed by adventitious base. However, given that the Ru analog, [Ru(CO)(NO)(PBu$^t_2$Me)$_2$]$^+$, produced no vinylidene species when reacted with PhCCH on a similar timescale, one could conclude that reduced electron density at the metal and thus reduced ability to *oxidatively add* alkyne (Ru *vs.* Os) has caused the differing reaction paths.

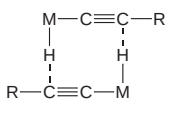
Summarizing the reactivity towards RCCH, [Os(CO)(NO)L$_2$]$^+$, **1**, did not activate a C–H bond when R = H; the reaction stops at the η^{2}acetylene form. When R = Ph, there is an equilibrium between η^2-alkyne and the hydrido alkynyl (favoring the η^2-alkyne) and these slowly convert to the final product vinylidene. *tert*-Butylacetylene is quickly and completely converted by **1** to the hydrido alkynyl and conversion to vinylidene is very fast at room temperature. Two things are thus apparent. First, the steric profile of incoming alkyne correlates well with the position of the equilibrium between the η^2 and oxidative addition products, the latter moving the bulky R group farther from the metal. Second, the subsequent conversion to vinylidene appears to correlate with the presence of hydrido alkynyl species. Other examples of d^8, Rh^I and Ir^I, metal complexes have been found to isomerize terminal acetylene to its vinylidene isomer.[3i,j,k,10] An analogous equilibrium between hydrido acetylide and the η^2-bound alkyne has been proven in the case of [RhCl(PPr$^i_3$)$_2$] with terminal alkynes. Both analogs, Rh and Ir, of these compounds have been proposed to isomerize to vinylidene from the hydrido acetylide species using a 1,3-hydrogen migration mechanism. These are important examples because they do *not* involve cationic species and polar, protic solvents.

1,2-Isomerization is not entirely excluded from the possible mechanisms for isomerization. However, the production of [Os(CCH$_2$)(CO)(NO)L$_2$]$^+$ from the double hydrolysis of [Os{CC(TMS)$_2$}(CO)(NO)L$_2$]$^+$ has proven the stability and kinetic persistence of this OsCCH$_2$ product. Therefore, the lack of observed isomerization from η^2-acetylene to vinylidene *and* the reverse for the case R = H must be explained by either an unusually high barrier for 1,2-hydrogen migration (relative to other η^2-alkynes) or the absence of oxidative addition of an acetylene C–H bond. The R group dependence of the kinetics and thermodynamics of these reactions is still not fully understood. Barrier heights for η^2-alkyne-to-vinylidene isomerization are decreased by steric bulk, both in the alkyne R group and in the phosphine ligands.[11] Werner and co-workers found in the reactions of RhCl(PPr$^i_3$)$_2$ with TMS acetylenes that the steric encumbrance of R in RCC(TMS) consistently predicted the facility of TMS migration, that is, greater bulk meant faster isomerization.[3] Despite this secondary support for 1,2-isomerizations, the presence here of an oxidative addition species for all systems that did undergo isomerization and the fact that in the *tert*-butylacetylene reaction, the hydrido alkynyl was the only species observed prior to isomerization, strongly indicates that 1,2-migrations are not involved with our system.

Conclusions

This study reveals that the cationic species Os(H)$_2$(NO)(CO)L$_2$$^+$ and OsH(C$_2$Ph)(NO)(CO)L$_2$$^+$ are sufficiently Brønsted acidic to be deprotonated by NEt$_3$. This is certainly not true of Ru(H)$_2$(CO)$_2$L$_2$.

While Ru(NO)(CO)L$_2$$^+$ does not react with PhCCH at 25 °C after 30 min, the higher reactivity of the osmium analog is clearly defined by our observations. This reaction is surprisingly complex, yet rich in mechanistic detail. The primary product is the η^2-alkyne adduct. This evolves in time at 25 °C to form the oxidative addition product OsH(C$_2$Ph)(NO)(CO)L$_2$$^+$, and subsequently the vinylidene isomer Os(CCHPh)(NO)(CO)L$_2$$^+$. Since this reaction can be demonstrated to occur in the presence of excess acid, this reaction cannot be base catalyzed. However, a recent high-level theoretical study finds that a bimolecular hydrogen transfer (**E**) can be easier than an intramolecular 1,3-hydrogen migration.[6] The results reported here show that the η^2-alkyne complex is the primary product of reaction of the alkyne with unsaturated Os(0), and that this adduct comes to thermal equilibrium with the hydrido phenylacetylide isomer faster than it begins to form the vinylidene isomer. Therefore, the phenylacetylene system does not allow us to determine whether the vinylidene isomer is formed directly from the η^2-PhCCH or the hydrido/acetylide species. Indeed, the η^2-HCCH analog shows no tendency at all to isomerize; no H migration is seen up to 60°. Unfortunately, we cannot distinguish whether the subsequently formed hydrido acetylide isomer is on the path to vinylidene, or whether it is a dead-end side reaction. On the other hand, the "isomerization-prone" alkyne with R = Ph does *not* oxidatively add to Ru(CO)$_2$(PBu$^t_2$Me)$_2$, but it does form an η^2-alkyne adduct,



E

and no isomerization to vinylidene is seen; this could be interpreted as the hydrido acetylide being a true intermediate.

Pairwise comparison of the $ML'(CO)(NO)L_2$ compounds for M = Ru and Os shows 20–40 cm^{-1} lower ν(CO) and ν(NO) values for M = Os. This confirms that osmium is more reducing than ruthenium in analogous compounds, a conclusion that reinforces the general trend in reactivity of $M(CO)(NO)L_2^+$ ions reported here. The ν(CO) and ν(NO) values for $OsX(CO)(NO)L_2$ are lower for the hydride than for the acetylide cases, which shows the greater σ-donor power of H than of C≡CPh. Also, the ν(NO) value of $Os(CCPh)(CO)(NO)L_2$, 1620 cm^{-1}, is so much higher than that (1539 cm^{-1}) in $OsCl(CO)(NO)L_2$ that we conclude the acetylide complex is trigonal bipyramidal, with linear NO and *trans* axial phosphines.

While the facile hydride fluxionality of $Os(H)_2(NO)(CO)L_2^+$ is atypical for octahedral complexes in general, there is ample precedent for *cis* dihydrides being fluxional.[12]

Acknowledgement

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References

1 M. Ogasawara, S. A. Macgregor, W. E. Streib, K. Folting, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1995, **117**, 8869.
2 (*a*) M. Ogasawara, D. J. Huang, W. E. Streib, J. C. Huffman, N. Gallego–Planas, F. Maseras, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc.*, 1997, **119**, 8642. (*b*) G. B. Richter–Addo and P. Legzdins, *Metal Nitrosyls*, Oxford University Press, New York, 1992.
3 (*a*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197. (*b*) M. A. Esteruelas, L. A. Oro and C. Valero, *Organometallics*, 1995, **14**, 3596. (*c*) D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet and P. H. Dixneuf, *Organometallics*, 1997, **16**, 3640. (*d*) R. Le Lagadec, E. Roman, L. Toupet, U. Müller and P. H. Dixneuf, *Organometallics*, 1994, **13**, 5030. (*e*) I. de los Rios, M. Jiménez–Tenorio, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 1997, **119**, 6529. (*f*) C. Bianchini, M. Peruzzini, A. Vacca and F. Zanobini, *Organometallics*, 1991, **10**, 3697. (*g*) P. Barbara, C. Bianchini, M. Peruzzini, A. Polo, F. Zanobini and P. Frediani, *Inorg. Chim. Acta*, 1994, **220**, 5. (*h*) A. B. Antonova and A. A. Ioganson, *Usp. Khim*, 1989, **68**, 1197. (*i*) J. Wolf, H. Werner, O. Serhadli and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 414. (*j*) F. J. García–Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 406. (*k*) A. Höhn, H. Otto, M. Dziallas and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1987, 852. (*l*) H. Werner, F. J. García–Alonso, H. Otto and J. Wolf, *Z. Naturforsch., Teil B*, 1988, **43**, 722. (*m*) H. Werner and U. Brekau, *Z. Naturforsch., Teil B*, 1989, **44** , 1438. (*n*) A. Höhn and H. Werner, *J. Organomet. Chem.*, 1990, **382**, 255. (*o*) H. Werner, A. Höhn and M. Schulz, *J. Chem. Soc., Dalton Trans.*, 1991, 777. (*p*) T. Rappert, O. Nürnberg, N. Mahr, J. Wolf and H. Werner, *Organometallics*, 1992, **11**, 4156. (*q*) H. Werner, M. Baum, D. Schneider and B. Windmüller, *Organometallics*, 1994, **13**, 1089. (*r*) H. Werner, T. Rappert, M. Baum and A. Stark, *J. Organomet. Chem.*, 1993, **459**, 319.
4 (*a*) K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 1970, 2149. (*b*) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.
5 M. Brookhart, B. Grant and A. F. Volpe, Jr., *Organometallics*, 1992, **11**, 3920.
6 Y. Wakatsuki, K. Nobuaki, H. Werner and K. Morokuma, *J. Am. Chem. Soc.*, 1997, **119**, 360.
7 J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.
8 M. P. Gamasa, J. Gimeno, E. Lastra and M. M. Blanca, *Organometallics*, 1992, **11**, 1373.
9 B. Buriez, I. D. Burns, A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton–Ely, *Organometallics*, 1999, **18**, 1504.
10 H. Werner and A. Höhn, *J. Organomet. Chem.*, 1984, **272**, 105.
11 J. R. Lomprey and J. P. Selegue, *J. Am. Chem. Soc.*, 1992, **114**, 5518.
12 B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Dalton Trans*, 1974, 981.

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