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Synthetic and thermochemical studies of reactions of the 16-electron ruthenium complex $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ with H_2, CH_3CN and CO

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Abstract

The 16-electron ruthenium complex $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**) has been prepared by chloride abstraction from $(Ph_2PNMeNMePPh_2)_2RuCl_2$ (**1**) with $AgBF_4$. The enthalpies of reaction of $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**) with H_2, CH_3CN and CO, leading to the formation of complexes $[(Ph_2PNMeNMePPh_2)_2RuCl(L)]BF_4$ ($L = H_2$ (**3**); CH_3CN, (**4**); CO (**5**)), have been measured by anaerobic calorimetry in CH_2Cl_2 at 30°C. These reactions are rapid and quantitative. The relative order of stability established for these complexes is **5** > **4** > **3**. Reactivity and thermochemistry of one alkyne, HCC^nBu, has also been investigated. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Thermochemistry; Ruthenium; Phosphine ligand; Unsaturated complex

1. Introduction

Thermochemical studies performed on organometallic systems have gained recognition as an area of research that can provide important insights into reactivity [1,2], bonding patterns [3] and direct the design of new metal-catalyzed transformations [4]. In recent years we have been interested in the thermochemical study of transition metal phosphine complexes [5,6](Eq. (1)):

$$Cp'Ru(COD)Cl_{(soln)} + 2PR_{3\,(soln)} \xrightarrow[30°C]{THF} Cp'Ru(PR_3)_2Cl_{(soln)} + COD_{(soln)} \qquad (1)$$

$Cp' = C_5H_5, C_5Me_5$; PR_3 = tertiary phosphine.

Furthermore, we have also determined the enthalpies of reactions involving coordinatively unsaturated 16-electron ruthenium complexes $Cp^*Ru(PR_3)X$ ($PR_3 = PCy_3, P^iPr_3$; $X = Cl, OCH_2CF_3$) and $Ru(CO)_2L_2$ ($L = P^iPr_3, P^tBu_2Me$ and PCy_3) (Eqs. (2)–(4)) [7].

$$Cp^*Ru(PR_3)X + 2PR'_3 \xrightarrow[30°C]{THF} Cp^*Ru(PR'_3)_2X + PR_3 \qquad (2)$$

$PR_3 = PCy_3, P^iPr_3$
$PR'_3 = PEt_3, P(OMe)_3$
$X = Cl, OCH_2CF_3$

$$Ru(CO)_2L_2 + L' \xrightarrow[30°C]{Toluene} Ru(CO)_2L_2 + L' \qquad (3)$$

$$Ru(CO)_2L_2 + PhCCH \xrightarrow[30°C]{Toluene} Ru(CO)_2L_2(H)(CCPh) \qquad (4)$$

$L = P^iPr_3, P^tBu_2Me, PCy_3$
$L' = MeNC, C_2Ph_2, CO$

Diphosphine modified ruthenium(II) complexes $[RuX(PP)_2]^+$ ($X = H, Cl$; PP = diphosphine ligands) represent an important class of 16-electron species. Studies of these compounds have shown that they are very reactive toward a variety of reagents, and in some instances are active catalysts for organic transformations [8]. Given that the bonding of small molecules to coordinatively unsaturated metal centers is fundamental to organometallic chemistry and homogenous catalysis, we have recently synthesized such a complex $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**1**) and investigated the thermochemistry of its reactions with catalytically relevant substrates: H_2, CH_3CN, CO and $HC{\equiv}CC^nBu$.

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2. Experimental section

2.1. General considerations

All manipulations involving organoruthenium complexes were performed under an atmosphere of argon using standard high vacuum or Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm oxygen and water. CH_2Cl_2 was distilled from CaH_2 and vacuum transferred into flame dried glassware prior to use. NMR spectra were recorded using either Varian Gemini 300 MHz or Unity 400 MHz spectrometer. IR were recorded using a Perkin-Elmer FTIR Model 2000 spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction [9] or the enthalpy of solution of KCl in water [10]. The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described [11] and typical procedures are described below. Only materials of high purity as indicated by IR and NMR spectroscopes were used in the calorimetric experiments. Experimental enthalpy data are reported with 95% confidence limits. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

2.2. Synthesis

The compounds $Ru(PPh_3)_3Cl_2$ [12] and $PPh_2PNMeNMePPh_2$ [13] were synthesized according to literature procedures. Experimental synthetic procedures, leading to isolation of complexes **1**–**6**, are reported below.

2.3. $(Ph_2PNMeNMePPh_2)_2RuCl_2$ (**1**)

$Ru(PPh_3)_3Cl_2$ (500 mg, 0.52 mmol) and $PPh_2PNMeNMePPh_2$ (445 mg, 1.04 mmol) were dissolved in toluene (15 ml) and the mixture was stirred for 16 h at room temperature (r.t.), during which time a pale-yellow precipitate formed. The solid was collected on a glass frit, washed with small amounts of toluene and diethyl ether, and dried under vacuum. Yield: 490 mg (92%).^{1}H-NMR (CD_2Cl_2): 2.70 (s, 12H, NMe), 6.60–7.40 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 123.3. EI MS: M$^+$ ion: Calc. for $C_{52}H_{52}Cl_2N_4P_4Ru$: 1027; Found: 1027.

2.4. $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**)

A suspension of complex **1** (1.04 g, 1.01 mmol) in CH_2Cl_2 (5 ml) was treated with $AgBF_4$ (197 mg, 1.01 mmol), and the mixture was stirred at r.t. for 60 h, whereupon the solution turned red and a precipitate of AgCl was formed. Insoluble materials were removed by filtration, and the solution was evaporated to dryness, affording a red solid which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 0.96 g (88%). ^{1}H-NMR (CD_2Cl_2): 2.17 (t, 6H, NMe), 2.93 (t, 6H, NMe), 6.80–8.00 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 114.4 (t, $J_{pp} = 27.9$ Hz), 129.8(t, $J_{pp} = 27.9$ Hz). Calc. for $C_{52}H_{52}BClF_4N_4P_4Ru$: C, 57.82; H, 4.85; N, 5.19. Found: C, 57.45; H, 4.68; N, 5.25.

2.5. $[(Ph_2PNMeNMePPh_2)_2RuCl(H_2)]BF_4$ (**3**)

A solution of **2** (50 mg, 0.046 mmol) in CH_2Cl_2 (5 ml) was saturated with H_2 and stirred for 1 h at r.t. On addition of diethyl ether, a white precipitate formed. The product was collected on a glass frit, washed with diethyl ether and dried under a stream of H_2. **3** is isolated as an off-white solid in a 64% Yield. ^{1}H-NMR (CD_2Cl_2): -12.00 (m, 2H, Ru–H_2), 2.62 (t, 12H, NMe), 6.50–9.00 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 113.0.

2.6. $[(Ph_2PNMeNMePPh_2)_2RuCl(CH_3CN)]BF_4$ (**4**)

Using a procedure analogous to the one described for **3**, **4** was isolated as a white solid in a 85% Yield. ^{1}H-NMR (CD_2Cl_2): 1.19 (s, 3H, CH_3CN), 2.71 (t, 12H, NMe), 6.76–7.60 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 111.5. IR (CH_2Cl_2): ν(CN) 2302 cm^{-1}.

2.7. $[(Ph_2PNMeNMePPh_2)_2RuCl(CO)]BF_4$ (**5**)

A solution of **2** (50 mg, 0.046 mmol) in CH_2Cl_2 (5 ml) was saturated with CO and stirred for 1 h at r.t. On addition of diethyl ether, a white precipitate formed. The product was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 38 mg (75%). ^{1}H-NMR (CD_2Cl_2): 2.70 (t, 12H, NMe), 6.92–7.60 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 109.5. IR (CH_2Cl_2): $\nu(C\equiv O)$ 1968 cm^{-1}. Calc. for $C_{53}H_{52}BClF_4N_4OP_4Ru$: C, 57.44; H, 4.73; N, 5.06. Found: C, 57.13; H, 4.55; N, 5.04.

2.8. $[(Ph_2PNMeNMePPh_2)_2RuCl(=C=CH^nBu)]BF_4$ (**6**)

Using a procedure analogous to the one described for **5**, **6** was isolated as an off-white solid in a 63% Yield. ^{1}H-NMR (CD_2Cl_2): 0.78 (t, $J = 7.2$ Hz, 3H, CH_3), 0.96 (m, 2H, CH_2). 1.01 (m, 2H, CH_2), 1.89 (dt, $J = 7.2$Hz, 2H, CH_2), 2.73 (t, 12H, NMe), 4.20 (m, 1H, CHBu); 7.02–7.56 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): 117.2. IR (CH_2Cl_2): ν(C=C) 1664 cm^{-1}. EI MS: M$^+$ ion: Calc. for $C_{58}H_{62}BClF_4N_4P_4Ru$: 1160; Found: 1160.

2.9. NMR titration

Prior to every set of calorimetric experiments involving a new reaction, an accurately weighed amount (± 0.1 mg) of the organoruthenium complex $[(Ph_2PNMeNMe-PPh_2)_2RuCl]BF_4$ (**2**) was placed in a Wilmad screw-capped NMR tube fitted with a septum, and CD_2Cl_2 was subsequently added. The solution was titrated with a solution of the reactant of interest by injecting the latter in aliquots through the septum with a microsyringe (for the reactions with CO and H_2, a CD_2Cl_2 solution saturated with H_2 or CO was added to the NMR tube), followed by vigorous shaking. The reactions were monitored by ^{1}H- and ^{31}P-NMR spectroscopy and the reactions were found to be rapid and quantitative, conditions necessary for accurate and meaningful calorimetric results. These criteria were satisfied for all organoruthenium reactions investigated.

2.10. Solution calorimetry. Calorimetric measurement for reaction between $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ and CH_3CN

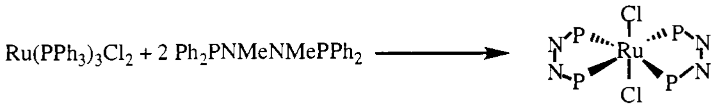
The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120°C, and then taken into the glovebox. A 20–30 mg sample of recrystallized $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**) was accurately weighed into the lower vessel, which was then closed and sealed with 1.5 ml of mercury. A total of 4 ml of a stock solution (0.5 ml of CH_3CN in 25 ml of CH_2Cl_2) was added and the remainder of the cell was assembled, removed from the glovebox and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organoruthenium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0°C (ca. 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h) the vessels were removed from the calorimeter. Conversion to $[(Ph_2PNMeNMePPh_2)_2RuCl(CH_3CN)]BF_4$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, -19.8 ± 0.2 kcal mol^{-1} represents the average of three individual calorimetric determinations. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study (for the reactions with CO and H_2, a CH_2Cl_2 solution saturated with H_2 or CO was used).

2.11. Structure determination of $[(Ph_2PNMeNMePPh_2)_2Ru(Cl)(CO)]BF_4$ (5)

Pale yellow crystals of **5** were obtained by slow evaporation of a methylene chloride solution of **5**. A single crystal having approximate dimensions $0.30 \times 0.24 \times 0.08$ mm was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo–K_α radiation at 113 K. Cell dimensions were determined by least-squares refinement of the measured setting angles of 30 reflections with $16° < 2\theta < 25°$. The structure was solved using direct methods (MULTAN80) and refined by full-matrix least-squares techniques. The crystallographic data are given in Table 2. Selected bond distances and angles are presented in Table 3 and the atomic coordinates in Table 4.

3. Results and discussion

The preparation of $(Ph_2PNMeNMePPh_2)_2RuCl_2$ (**1**) from $Ru(PPh_3)_3Cl_2$ and two equivalents of $Ph_2PNMeNMePPh_2$ proceeds in high yield at r.t. (Eq. (5)). The *trans* arrangement of the two chlorine atoms in complex **1** was assigned on the basis of $^{31}P\{^1H\}$-NMR, where a singlet at δ 123.3 ppm was observed, consistent with four equivalent phosphorus nuclei. Subsequent chloride abstraction from **1** with $AgBF_4$ affords the 16-electron complex $(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**) (Eq. (6)). Complex **2** was characterized by ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy and elemental analysis,. The $^{31}P\{^1H\}$-NMR spectrum of **2** exhibits two triplets centered at δ 114.4 and δ 129.8 ppm with $^2J_{pp} = 27.9$ Hz, indicating that **2** has a trigonal–bipyramidal structure. Accordingly, the ^{1}H-NMR spectrum of **2** shows two triplets centered at δ 2.17 and 2.93 ppm, which are attributable to the diastereotopic NMe groups in the coordinated $Ph_2PNMeNMePPh_2$ ligands.



(5)

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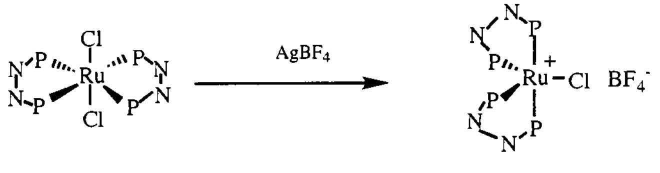


(6)

1 2

PNNP = $Ph_2PNMeNMePPh_2$

Table 1
Enthalpies of reaction (kcal mol^{-1}) for: $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_{4\,(s)} + L_{(soln)} \xrightarrow[30°C]{CH_2Cl_2} [(Ph_2PNMeNMePPh_2)_2Ru(L)Cl]BF_{4\,(soln)}$

L	$-\Delta H^{a}_{rxn}$
CH_2Cl_2	1.7 (0.2)
H_2	10.3 (0.3)
$HCC^{n}Bu$	16.1 (0.1)
CH_3CN	19.8 (0.2)
CO	34.5 (0.3)

[a] Enthalpies of reaction are reported with 95% confidence limits.

Thermochemical studies are based on the reactions shown in Scheme 1, and enthalpy data are presented in Table 1. These reactions are rapid and quantitative at r.t. ^{1}H- and ^{31}P{^{1}H}-NMR spectra are very diagnostic of the quantitative nature of these addition reactions. The ^{31}P{^{1}H}-NMR spectra of complexes $[(Ph_2PNMeNMePPh_2)_2RuCl(L)]BF_4$ (L = H_2, **3**; CH_3CN, **4**; CO, **5**; =C=C(H)Bu^n, **6**), all exhibit a singlet at about δ 115 ppm, indicating that the chloride and the ligand L are in *trans* positions. In the ^{1}H-NMR spectra of **3**–**6**, a triplet was observed at about δ 2.7 ppm, corresponding to the equivalent NMe groups in the coordinated $Ph_2PNMeNMePPh_2$ ligands.

Table 2
Crystallographic data for 5

Empirical formula	$C_{53}H_{52}BClF_4N_4OP_4Ru \cdot CH_2Cl_2$
Formula weight	1193.12
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.2502(4)
b (Å)	12.6994(5)
c (Å)	19.6998(7)
α (°)	85.2020(10)
β (°)	88.4840(10)
γ (°)	70.0030(10)
V (Å^3)	2635.6(2)
Z	2
$D_{calc.}$ (g cm^{-3})	1.503
Absorption coefficient (cm^{-1})	0.629
F(000)	1220
Crystal size (mm)	0.30 × 0.24 × 0.08
θ range for data collection (°)	1.71–35.97
Index ranges	$-17 \leq h \leq 17$, $-20 \leq k \leq 15$, $-29 \leq l \leq 31$
No. of collected reflections	28217
Independent reflections	19832 ($R_{int} = 0.0389$)
Refinement method	Full-matrix least-squareson F^2
Data/restraints/parameters	19832/1/683
Goodness of fit on F^2	1.244
Final R index [$I > 2\sigma(I)$]	$R_1 = 0.0632$, $wR_2 = 0.1218$
R indices (all data)	$R_1 = 0.0827$, $wR_2 = 0.1320$
Largest difference peak and hole (e Å^{-3})	1.128 and -1.219

The importance of dihydrogen coordination as a first step of catalytic hydrogenation cannot be overstated [14]. A large body of work has focused on this fundamental issue [15]. In spite of this, few thermochemical studies quantifying the enthalpy of H_2 binding to organometallic moieties have been reported. In the present system, the enthalpy of reaction involving **2** and H_2 have been measured by solution calorimetry. A reaction enthalpy of -8.6 kcal mol^{-1} indicates that the Ru–H_2 interaction in $[(Ph_2PNMeNMePPh_2)_2RuCl(H_2)]BF_4$ (**4**) is a fairly weak one [16]. This result is consistent with the observations that H_2 is readily removed from **4** in vacuo, and supports the notion that hydrogen is a weak binding ligand. Furthermore, this value is close to the reaction enthalpies of H_2 binding to the $M(CO)_3(PCy_3)_2$ (M = Cr, Mo, W) complexes (Eq. (10)) [15].

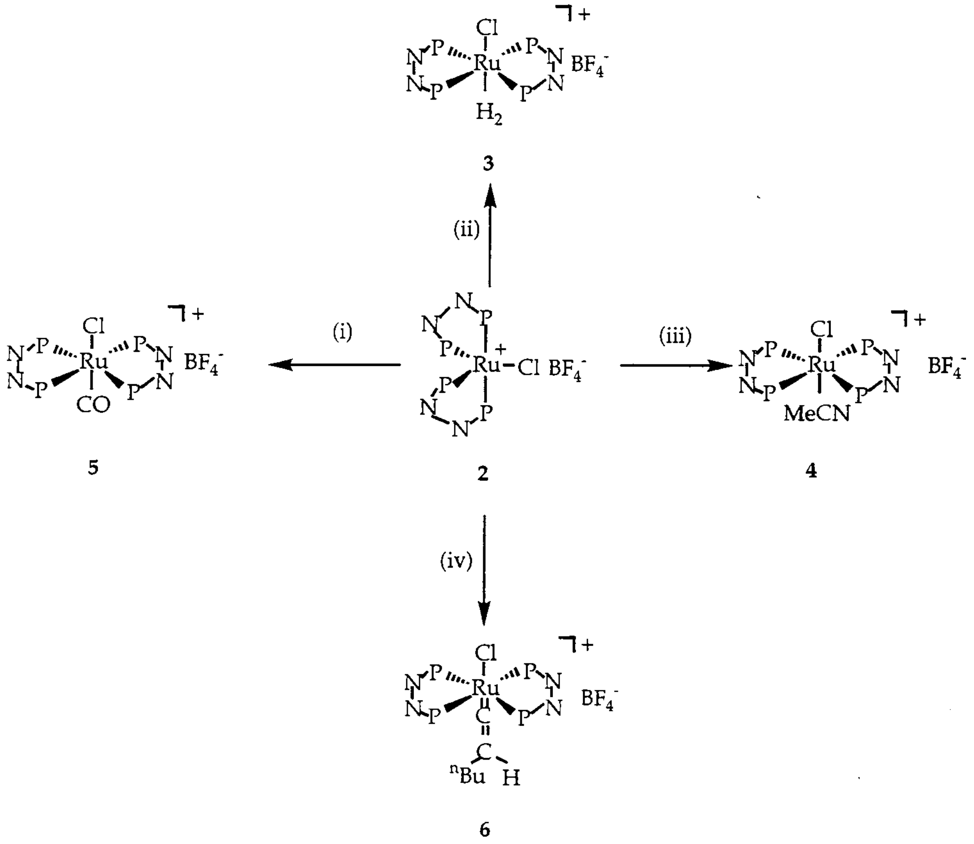
$$M(CO)_3(PCy_3)_2 + H_2 \rightarrow M(CO)_3(PCy_3)_2(H_2) \qquad (10)$$

M = Cr, $\Delta H = -7.3$ kcal mol^{-1}
M = Mo, $\Delta H = -6.5$ kcal mol^{-1}
M = W, $\Delta H = -10.0$ kcal mol^{-1}

Acetonitrile is weakly bound to the ruthenium center in $[(Ph_2PNMeNMePPh_2)_2RuCl(CH_3CN)]BF_4$ (**5**). The reaction enthalpy of CH_3CN with $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ is -19.8 kcal mol^{-1}, significantly higher than H_2. This value is about 5 kcal mol^{-1} lower than the reaction enthalpy of CH_3CN with the unsaturated 16-electron tungsten (d^6) complex $W(CO)_3(dppm)$ (Eq. (11)) [17] and 3 kcal mol^{-1} higher than the reaction of CH_3CN with $W(CO)_3(PCy_3)_2$ (Eq. (12)), due to the W···H–C agostic interaction in $W(CO)_3(PCy_3)_2$ ([15]a). A more accurate value for the simple occupa-

Table 3
Selected bond distances (Å) and bond angles (°) for **5**

Bond lengths			
Ru(1)–C(54)	1.839(8)	N(1)–N(2)	1.425(3)
Ru(1)–P(2)	2.3803(7)	N(1)–C(25)	1.469(4)
Ru(1)–P(1)	2.3964(7)	O(1)–C(54)	1.172(8)
Ru(1)–Cl(4A)	2.433(3)	P(2)–C(13)	1.829(3)
P(1)–N(1)	1.709(3)	P(2)–C(19)	1.830(3)
P(1)–C(7)	1.819(3)	N(2)–C(26)	1.467(4)
P(l)–C(1)	1.826(3)	P(2)–N(2)	1.683(3)
Bond angles			
C(54)–Ru(1)–P(2A)	93.9(2)	P(2)–Ru(1)–P(2A)	180.0
C(54)–Ru(1)–P(2)	86.1(2)	P(1)–Ru(1)–P(1A)	180.0
C(54)–Ru(1)–P(1A)	92.6(2)	C(54)–Ru(1)–Cl(4A)	177.2(2)
P(2)–Ru(l)–P(1A)	100.45(2)	P(2)–Ru(1)–Cl(4A)	96.37(4)
C(54)–Ru(1)–P(1)	87.4(2)	P(1A)–Ru(1)–Cl(4A)	85.74(4)
P(2)–Ru(1)–P(1)	79.55(2)	P(1)–Ru(1)–Cl(4A)	94.26(4)
Ru(1)–P(1)–N(1)	107.05(9)	N(2)–N(1)–P(1)	110.4(2)
Ru(1)–P(2)–N(2)	106.60(9)	N(1)–N(2)–P(2)	122.9(2)
N(2)–N(1)–C(25)	113.2(2)	N(1)–N(2)–C(26)	114.7(2)
Ru(1)–C(54)–0(1)	177.8(8)		



PNNP = $Ph_2PNMeNMePPh_2$

(i) CO, CH_2Cl_2 (ii) H_2, CH_2Cl_2

(iii) MeCN, CH_2Cl_2 (iv) HCC^nBu, CH_2Cl_2

Scheme 1.

tion of the vacant site in this latter W system is 25.3 kcal mol^{-1} since the agostic interaction has been estimated as 10 kcal mol^{-1}.

$$W(CO)_3(dppm) + CH_3CN \rightarrow W(CO)_3(dppm)(CH_3CN) \quad (11)$$

$\Delta H = -23.5$ kcal mol^{-1}

$$W(CO)_3(PCy_3)_2 + CH_3CN \rightarrow W(CO)_3(PCy_3)_2(CH_3CN) \quad (12)$$

$\Delta H = -15.3$ kcal mol^{-1}

In order to gauge the electron donating properties of the metal center in the present system, the reaction enthalpy of CO with the unsaturated 16-electron complex $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ (**2**) was measured as -35.6 kcal mol^{-1}, the most exothermic in this system. This value is about 3 kcal mol^{-1} larger than the energy of CO addition to $Ru(CO)_4$ (Eq. (7)) [18] and 4–9 kcal mol^{-1} larger than the values obtained in the unsaturated d^8 $Ru(CO)_2L_2$ system (Eq. (8)) ([7]d)

$$Ru(CO)_4 + CO \rightarrow Ru(CO)_5 \quad (7)$$

$\Delta H = -33$ kcal mol^{-1}

$$Ru(CO)_2L_2 + CO \rightarrow Ru(CO)_3L_2 \quad (8)$$

$L = P^tBu_2Me$; $\Delta H = -26.2$ kcal mol^{-1}
$L = PCy_3$; $\Delta H = -28.9$ kcal mol^{-1}
$L = P^iPr_3$; $\Delta H = -31.4$ kcal mol^{-1}

It should also be pointed out that the value reported by Scaiano and co-workers for the dissociation of Ru–CO in the very electron-rich complex $Ru(Me_2PCH_2CH_2PMe_2)_2CO$ of 43 kcal mol^{-1} [19] is 7 kcal mol^{-1} higher than the Ru–CO bond enthalpy value measured in complex **5**. These facts suggest that steric and electronic effects of the ancillary ligands and the oxidation state of the ruthenium center must play some role in dictating the magnitude of the bond enthalpy of Ru–CO. Hoff and co-workers have studied the bonding of CO to the unsaturated d^6 tungsten complex $W(CO)_3(PCy_3)_2$ (Eq. (9)), where the reaction enthalpy was determined to be -30 kcal mol^{-1}. This

Table 4
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (A^2×10^3) for 5

	x	y	z	U_{eq}^{a}
Ru(1)	0	5000	0	9(1)
Cl(1)	581(1)	525(1)	2530(1)	37(1)
P(1)	1038(1)	4721(1)	−1082(1)	12(1)
N(1)	974(2)	3487(2)	−1335(1)	16(1)
C(1)	2740(3)	4451(2)	−1091(1)	14(1)
0(1)	−2305(6)	4893(6)	−693(3)	20(1)
B(1)	−3188(4)	9513(3)	2655(2)	26(1)
F(1)	−2865(2)	10 173(2)	2127(1)	34(1)
Ru(2)	5000	5000	5000	9(1)
P(2)	735(1)	3003(1)	29(1)	12(1)
N(2)	1183(3)	2668(2)	−770(1)	19(1)
C1(2)	1907(1)	−1646(1)	1992(1)	33(1)
C(2)	3579(3)	3461(3)	−1331(2)	19(1)
O(2)	7415(6)	5030(4)	4310(3)	20(1)
F(2)	−3958(3)	10 195(3)	3115(1)	53(1)
P(3)	4051(1)	5333(1)	3898(1)	12(1)
N(3)	4150(2)	6579(2)	3534(1)	14(1)
C(3)	4880(3)	3235(3)	−1295(2)	26(1)
Cl(3)	6879(2)	5092(1)	4410(1)	14(1)
F(3)	−3809(3)	8883(3)	2380(2)	54(1)
P(4)	4290(1)	7008(1)	4869(1)	11(1)
N(4)	3922(2)	7372(2)	4039(1)	15(1)
C(4)	5354(3)	3990(3)	−1043(2)	28(1)
Cl(4)	−1815(2)	4857(2)	−580(1)	14(1)
F(4)	−2082(3)	8842(3)	2978(2)	70(1)
C(5)	4522(3)	5004(3)	−828(2)	24(1)
C(6)	3221(3)	5226(3)	−840(2)	19(1)
C(7)	433(3)	5667(2)	−1836(1)	14(1)
C(8)	−861(3)	6305(3)	−1888(1)	17(1)
C(9)	−1340(3)	6972(3)	−2482(2)	19(1)
C(10)	−543(3)	7008(3)	−3029(2)	21(1)
C(11)	742(3)	6392(3)	−2975(2)	23(1)
C(12)	1234(3)	5722(3)	−2383(1)	19(1)
C(13)	−407(3)	2305(2)	278(2)	16(1)
C(14)	−1022(3)	1974(3)	−222(2)	22(1)
C(15)	−1928(3)	1474(3)	−36(2)	26(1)
C(16)	−2212(3)	1302(3)	644(2)	23(1)
C(17)	−1611(3)	1644(2)	1145(2)	21(1)
C(18)	−716(3)	2149(2)	964(2)	18(1)
C(19)	2167(3)	2181(2)	511(1)	15(1)
C(20)	2285(3)	1220(3)	947(2)	23(1)
C(21)	3431(3)	629(3)	1273(2)	28(1)
C(22)	4474(3)	975(3)	1167(2)	28(1)
C(23)	4366(3)	1910(3)	723(2)	22(1)
C(24)	3222(3)	2506(3)	396(2)	18(1)
C(25)	13(3)	3443(3)	−1812(2)	23(1)
C(26)	1956(3)	1523(3)	−920(2)	24(1)
C(27)	2356(3)	5581(2)	3880(1)	14(1)
C(28)	1505(3)	6570(3)	3568(2)	20(1)
C(29)	210(3)	6750(3)	3587(2)	25(1)
C(30)	−240(3)	5945(3)	3892(2)	27(1)
C(31)	609(3)	4942(3)	4184(2)	23(1)
C(32)	2899(3)	4760(3)	4184(2)	17(1)
C(34)	3851(3)	4357(3)	2704(2)	19(1)
C(35)	4311(3)	3610(3)	2205(2)	23(1)
C(36)	5555(3)	2881(3)	2230(2)	22(1)
C(37)	6360(3)	2917(3)	2743(2)	18(1)
C(38)	5917(3)	3673(2)	3237(1)	15(1)
C(39)	4659(3)	4388(2)	3230(1)	13(1)
C(39)	5408(3)	7700(2)	5065(1)	14(1)
C(40)	6102(3)	8011(3)	4534(2)	20(1)
C(41)	6949(3)	8541(3)	4662(2)	25(1)
C(42)	7113(3)	8784(3)	5323(2)	23(1)
C(43)	6439(3)	8472(3)	5854(2)	20(1)
C(44)	5598(3)	7922(2)	5733(2)	17(1)
C(45)	2801(3)	7821(2)	5267(1)	14(1)
C(46)	2633(3)	8743(2)	5648(2)	17(1)
C(47)	1430(3)	9344(3)	5887(2)	21(1)
C(48)	394(3)	9053(3)	5741(2)	21(1)
C(49)	550(3)	8148(3)	5355(2)	19(1)
C(50)	1743(3)	7529(2)	5127(1)	16(1)
C(51)	5214(3)	6583(3)	3078(2)	21(1)
C(52)	3250(3)	8529(2)	3778(2)	22(1)
C(54)	−1419(7)	4957(6)	−423(4)	14(1)
C(55)	6496(7)	5016(5)	4576(3)	12(1)
C(56)	433(4)	−661(4)	2192(3)	44(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

lower value is attributed to the presence of the W···H–C agostic interaction [20]. A value of −40 kcal mol^{-1} is more representative of the true binding of CO to the coordinatively unsaturated fragment.

$$W(CO)_3(PCy_3)_2 + CO \rightarrow W(CO)_4(PCy_3)_2 \qquad (9)$$

$\Delta H = -30$ kcal mol^{-1}

We note that no agostic interaction is observed in the 16-electron complexes [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)RuCl]BPh$_4$ ([8]d) and [(Cy$_2$PCH$_2$CH$_2$PCy$_2$)RuCl]PF$_6$ ([8]c) in the solid state. Given that Ph$_2$PNMeNMePPh$_2$ is most likely isosteric with Ph$_2$PCH$_2$CH$_2$PPh$_2$, there should be no agostic in complex [(Ph$_2$PNMeNMePPh$_2$)$_2$RuCl]BF$_4$ (**2**).

In order to verify bond length and bond angle variations as a function of ancillary ligation, and how these relate to enthalpy data, a single crystal diffraction study was carried out on complex **5**. An ORTEP is presented in Figs. 1 and 2. The metric parameters for **5**, listed in Table 3, allow comparisons with reported structures of [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Ru(CO)Cl]BPh$_4$ [21]. The Ru–P average distances in these two structures are 2.3883(7) in **5** and 2.430(1) Å in the diphos complex. The other significant difference is the Ru–C (from CO) distance, 1.839(8) (for **5**) and 1.771(17) Å for the diphos complex. The Ru–Cl and C–O bond distances in the two complexes are the same within reported estimated standard deviation values (estimated S.D.). The notable bond distance differences in the Ru–P and Ru–C parameters provide information about the electron donor properties of the two phosphine ligands. It appear that in this system the Ph$_2$PNMeNMePPh$_2$ ligand behaves as a better donor than diphos. The shorter Ru–P bond distances in **5** are a reflection of better Ru–P orbital overlap resulting in higher electron density at the metal center which in turn allows for a better

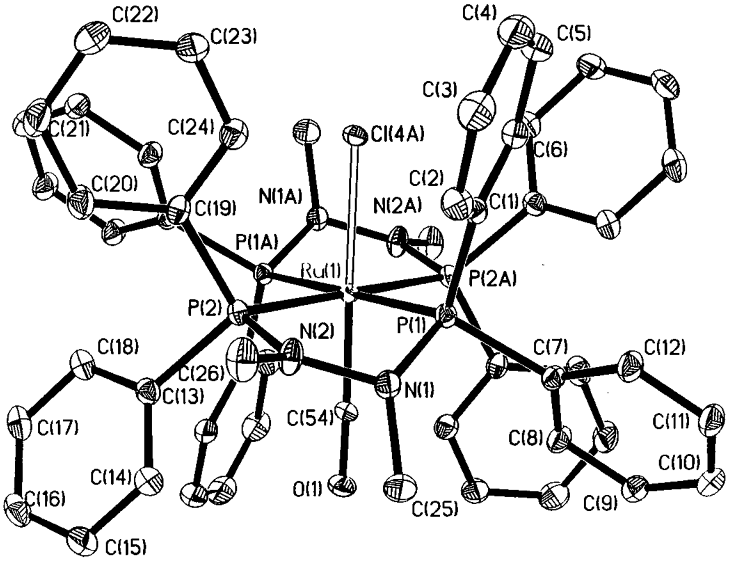


Fig. 1. ORTEP of $[(Ph_2PNMeNMePPh_2)_2RuCl(CO)]^+$. Ellipsoids drawn at 50% probability.

backdonation into the carbonyl π^* orbitals reflected in a longer Ru–C bond distance. The carbonyl IR data for **5** (1968 cm^{-1}) and the diphos complex (1973 cm^{-1}) also support the conclusion of the metric parameter analysis. This better donor behavior of $Ph_2PNMeNMePPh_2$ versus diphos is in contrast to the donor trend recently studied in the Cp′Ru(COD)Cl systems, where diphos was gauged as an equal or better donor [22]. Ancillary ligands obviously must be the cause of this reversal for the phosphine donor capability.

$$Cp'Ru(COD)Cl_{(soln)} + PP_{(soln)} \xrightarrow[30°C]{THF} Cp'Ru(PP)Cl_{(soln)} + COD_{(soln)} \qquad (13)$$

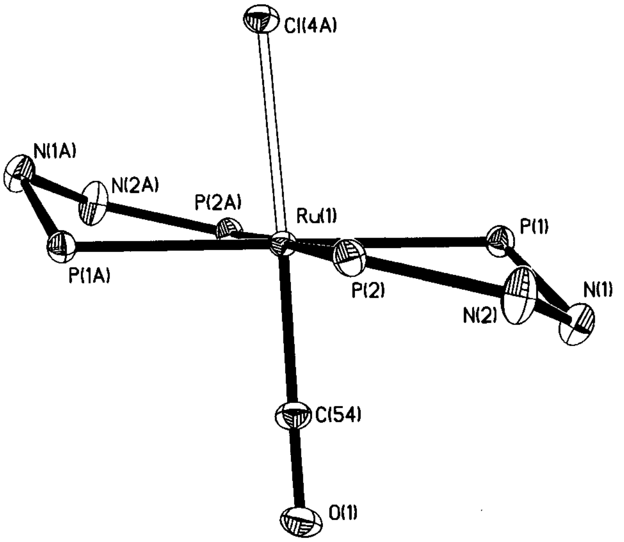


Fig. 2. The inner coordination sphere and chelate rings of $[(Ph_2PNMeNMePPh_2)_2RuCl(CO)]^+$.

Cp′	PP	$-\Delta H$ (kcal mol^{-1})
C_5H_5	$Ph_2PNMeNMePPh_2$	29.7(4)
C_5H_5	Diphos	30.5(2)
C_5Me_5	$Ph_2PNMeNMePPh_2$	22.6(2)
C_5Me_5	Diphos	29.8(2)

Given the great importance of M=C=C species in selective catalytic transformations of terminal alkynes [23], the reaction enthalpy of $HC{\equiv}C^nBu$ with $[(Ph_2PNMeNMePPh_2)_2RuCl]BF_4$ was also measured [24]. The heat of this reaction was determined to be -14.4 kcal mol^{-1}. As few data are available concerning this type of reaction, we note that this value is almost the same as that of the reaction of $Ru(CO)_2(P^iPr_3)_2$ with $PhC{\equiv}CPh$ (Eq. (14)) ([7]c) but much lower than that of the oxidative addition reaction of $Ru(CO)_2(P^iPr_3)_2$ with $HC{\equiv}CPh$ (Eq. (15)) ([7]c).

$$Ru(CO)_2(P^iPr_3)_2 + PhCCPh \rightarrow Ru(CO)_2(P^iPr_3)_2(PhCCPh) \qquad (14)$$

$$\Delta H = -14.7 \text{ kcal mol}^{-1}$$

$$Ru(CO)_2(P^iPr_3)_2 + HCCPh \rightarrow Ru(CO)_2(P^iPr_3)_2(H)(CCPh) \qquad (15)$$

$$\Delta H = -24.1 \text{ kcal mol}^{-1}$$

The thermochemical analysis for the formation of the vinylidene is complex since a number of bonds are made and broken in the generation of the final product. It is clear that the enthalpy of reaction represents the overall driving force for vinylidene formation yet it

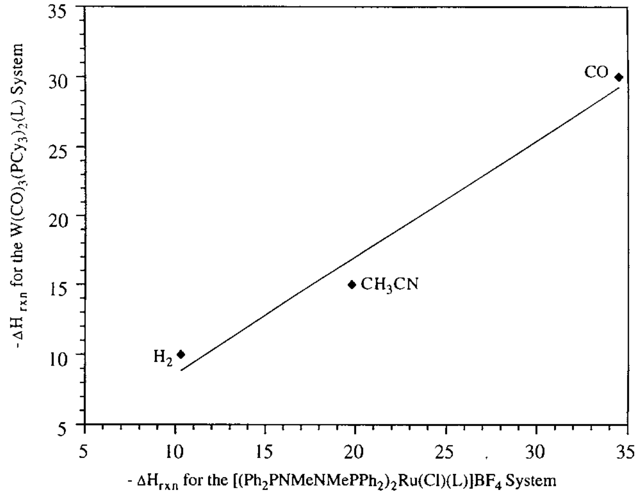


Fig. 3. Enthalpies of reaction of $W(CO)_3(PCy_3)_2(L)$ (kcal mol^{-1}) versus $[(Ph_2PNMeNMePPh_2)_2Ru(Cl)(L)]BF_4$ (kcal mol^{-1}); slope = 0.75, $R = 0.99$.

cannot be directly compared to simple adduct formation such as in the case of dihydrogen, acetonitrile and CO.

The enthalpy trend observed in this reaction system is $CO > CH_3CN > H_2$. When the enthalpy data of the present ruthenium system and that of the $W(CO)_3(PCy_3)_2(L)$ ($L = CO$, CH_3CN and H_2) system are compared, an interesting linear correlation is established (Fig. 3). This trend is obtained in spite of the fact that these two systems have different metal centers, ancillary ligation, oxidation state and the added agostic interaction in the W system. The correlation suggests that in spite of all these fundamental differences, the two systems respond to incoming ligand in a similar fashion.

4. Supplementary material available

Tables of atomic coordinates, selected bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for complex **5** are available upon request from the corresponding author.

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