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Synthesis and reactivity of η^6-arene ruthenium anilide complexes

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Abstract—The compounds, (η^6-C_6Me_6)Ru(PMe_3)(R)(NR′R″); (R=Ph, R′=H, R″=Ph, **3**; R=Me, R′=H, R″=Ph, **4**; R=Ph, R′=H, R″=*p*-tol, **5**; R=Me, R′=Me, R″=Ph, **6**) are synthesized through the interaction of (η^6-C_6Me_6)Ru(PMe_3)(R)(I) and the corresponding anilide salt, KNR′R″ in THF at low temperature. The reactions between these complexes and the unsaturated electrophilic reagents, CO_2 and dimethylacetylene dicarboxylate (DMAD) have been described. The typical reaction involves net insertion of the electrophile into the Ru anilide bond. Complex **6** reacts with H_2O giving the hydroxide complex, **11**, which reacts with CO_2 giving the bicarbonato complex, **12**. The X-ray crystal structure of **3** is reported. Compound **3** crystallizes in the monoclinic space group, $P2_1/n$, $a = 12.013(2)$ Å, $b = 16.700(3)$ Å, $c = 12.414(1)$ Å, $\beta = 97.35(2)$, $V = 2470.0(7)$ Å^3 and $Z = 4$. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: η^6-arene ruthenium anilide complexes; unsaturated electrophilic reagents; CO_2; DMAD.

We have been interested in the chemistry of late (group 8–10) transition metal amide complexes to investigate their reactivity and to examine the possibility of using them in stoichiometric or catalytic C—N bond forming reactions. The relative scarcity [1] of ruthenium compounds of this type sparked our interest in their chemistry. Our attention has been focused on the (η^6-C_6Me_6)Ru(PMe_3)(R)(NHR) class of compounds because of their ease of preparation and the fact that they are isoelectronic with the Cp*Ir(PMe_3)(R)X (X = NHR, OR, etc.) compounds which have been demonstrated to participate in an interesting array of reactions [2]. Furthermore, the chemistry of (η^6-C_6Me_6)Ru(PMe_3)(Ph)NHPh can be compared with other 18 e^- group 8 anilide and imido complexes such as $(PMe_3)_4$Ru(H)(NHPh)[1h] and (*p*-Cym)OsNR [3]. In this paper we describe the synthesis, and characterization of a series of arene Ru anilide complexes. The reactivity of these molecules with the unsaturated electrophiles, CO_2 and dimethylacetylene dicarboxylate (DMAD) are also reported. The reaction of a hydroxide derivative with CO_2 to give a bicarbonato complex is also described.

EXPERIMENTAL

All procedures were performed using either Schlenk or dry box techniques, under an inert atmosphere of either argon or nitrogen. Pentane and diethyl ether (Et_2O) were distilled from sodium/benzophenone and subsequently degassed. Methylene chloride was distilled from P_2O_5 and degassed. Tetrahydrofuran (THF) was dried by refluxing over potassium metal prior to distillation and then degassed after distillation. Deuterated solvents were dried over molecular sieves and degassed prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VXR-300 (300 MHz), or a General Electric QE-300 (300 MHz) spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to residual proton signals in the solvent and are reported relative to TMS; shifts for ^{31}P spectra are reported relative to external 85% H_3PO_4. Elemental analyses were performed by the University of Florida Analytical Services or Atlantic Microlab, Inc., Norcross, Georgia. Infrared spectra were recorded on a Perkins Elmer 1200 series spectrometer from KBr pellets which were prepared in an inert atmosphere glove box. Mass spectroscopy data were obtained with a Finnigan 4500 Gas Chromatograph/Mass Spectrometer using FAB techniques.

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The following compounds were purchased from Aldrich Chemical Co., and were used without further purification: dimethylacetylene dicarboxylate, phenyl lithium, methyl lithium, sodium iodide, and para-toluidine. Aniline and *N*-methyl aniline were distilled from sodium metal.

The potassium amides were synthesized by reacting the appropriate aniline and KH in THF, with KN(Me)Ph being prepared by modified literature procedures [4]. (η^6-C_6Me_6)Ru(PMe_3)Cl_2 was prepared according to literature methods [5], and (η^6-C_6Me_6)Ru(PMe_3)I_2 was prepared by ion exchange with NaI and (η^6-C_6Me_6)Ru(PMe_3)Cl_2 under reflux in acetone following the procedure used for the synthesis of Cp*Rh(PMe_3)I_2 [6].

Preparation of (η^6-C_6Me_6)Ru(PMe_3)(Ph)I (**1**)

To a stirring solution of (η^6-C_6Me_6)Ru(PMe_3)I_2 (1.037 g, 1.748 mmol) in 75 ml of THF was added dropwise 1.07 ml of a 1.8 M solution of LiPh in toluene/Et_2O (1.9 mmol). The solution immediately turned from purple to orange-red. After 45 min the solvent was removed under reduced pressure to leave an orange-red oil. The product was extracted with Et_2O until the extracts were colorless. The combined extracts were reduced in volume and cooled to −20°C giving deep red crystals of **1** (0.599 g, 1.102 mmol) in 63% yield. Anal. Calc. for $C_{21}H_{32}IPRu$: C, 46.41; H, 5.94. Found: C, 46.11; H, 5.95.

Preparation of (η^6-C_6Me_6)Ru(PMe_3)(Me)I (**2**)

To a stirring solution of (η^6-C_6Me_6)Ru(PMe_3)I_2 (3.50 g, 5.90 mmol) in 125 ml of THF was added dropwise 5.15 ml of a 1.26 M solution of LiMe in Et_2O (6.49 mmol). The solution immediately turned from purple to orange-red. After 45 min the solvent was removed under reduced pressure to leave a red oil. The product was extracted with Et_2O until the extracts were colorless. The combined extracts were reduced in volume and cooled to −20°C giving deep red crystals of **2** (2.12 g, 4.40 mmol) in 75% yield. Anal. Calc. for $C_{16}H_{30}IPRu$: C, 39.93; H, 6.28. Found: C, 39.04; H, 6.21. HRMS (FAB) (Calc.): 466.993 $(M\text{-}CH_3)^+$. (Found): 467.010 $(M\text{-}CH_3)^+$.

Preparation of (η^6-C_6Me_6)Ru(PMe_3)(NHPh)(Ph) (**3**)

To a cold (−78°C) stirring solution of **1** (0.730 g, 1.436 mmol) in 100 ml of THF was added a solution of KNHPh (0.264 g, 2.015 mmol) in 25 ml of THF. After 45 min the reaction mixture was allowed to come to room temperature, whereupon it slowly turned from clear red to brown with white precipitates. After stirring 2 h longer, the solvent was removed under reduced pressure to leave a sticky solid. The product was extracted with Et_2O until the extracts were colorless. The combined extracts were reduced in volume and cooled to −50°C giving deep red crystals of 3 (0.404 g, 0.795 mmol) in 55% yield. IR (KBr): 3330.6 cm^{-1} ($\nu_{N\text{-}H}$). Anal. Calc. for $C_{27}H_{38}NPRu$: C, 63.74; H, 7.53; N, 2.75. Found: C, 62.85; H, 7.58; N, 2.67. HRMS (FAB) (Calc.): 509.1779 $(M+1)^+$. (Found): 509.1659 $(M+1)^+$.

Preparation of (η^6-C_6Me_6)Ru(PMe_3)(NHPh)(Me) (**4**)

To a cold (−78°C) stirring solution of **2** (0.320 g, 0.665 mmol) in 50 ml of THF was added a solution of KNHPh (0.31 g, 0.997 mmol) in 25 ml of THF. After 45 min the reaction mixture was allowed to come to room temperature, whereupon it slowly turned from clear red to red-brown with white precipitates. After stirring 2 h longer, the solvent was removed under reduced pressure to leave a sticky solid. The product was extracted with Et_2O until the extracts were colorless. The combined extracts were reduced in volume and cooled to −50°C giving large, opaque red crystals of **5** (0.320 g, 0.718 mmol) in 72% yield. IR (KBr): 3329.7 cm^{-1} ($\nu_{N\text{-}H}$). Anal. Calc. for $C_{22}H_{36}NPRu$: C, 59.17; H, 8.13; N, 3.14. Found: C, 59.25; H, 8.18; N, 3.10.

Preparation of (η^6-C_6Me_6)Ru(PMe_3)($NHC_6H_4CH_3$)(Ph) (**5**)

To a cold (−78°C) stirring solution of **1** (0.980 g, 1.875 mmol) in 75 ml of THF was added a solution $KNHC_6H_4CH_3$ (0.393 g, 2.705 mmol) in 30 ml of THF. After 30 min the reaction mixture was allowed to come to room temperature, whereupon it slowly turned from clear red to orange-brown with white precipitates. After stirring 1 h longer, the solvent was removed under reduced pressure to leave a solid. The product was extracted with diethyl ether until the extracts were colorless. The combined extracts were reduced in volume and cooled to −50°C giving powdery orange crystals of **8** (0.608 g, 1.163 mmol) in 62% yield. IR (KBr): 3361.4 cm^{-1} ($\nu_{N\text{-}H}$). Anal. Calc. for: $C_{28}H_{40}NPRu$ C, 64.34; H, 7.71; N, 2.68. Found: C, 64.26; H, 7.72; N, 2.63.

Preparation of (η^6-C_6Me_6)Ru(PMe_3)(NMePh)(Me) (**6**)

To a cold (−78°C) stirring solution of **2** (0.250 g, 0.519 mmol) in 40 ml of THF was added a solution of KNMePh (0.113 g, 0.778 mmol) in 25 ml of THF. After 45 min the reaction mixture was allowed to come to room temperature, whereupon it slowly turned from clear red to red-brown with white precipitates. After stirring 2 h longer, the solvent was removed under reduced pressure to leave a solid. The product was easily extracted with a small volume (25 ml) of diethyl ether. The extract was reduced in volume and cooled to -50°C giving large, red crystals of **6** (0.130 g, 0.282 mmol) in 54% yield. Anal. Calc. for $C_{23}H_{38}N$-PRu: C, 59.98; H, 8.32; N, 3.04. Found: C, 59.77; H, 8.28; N, 2.94.

Reaction of **3** *with carbon dioxide. Synthesis of* (η^6-C_6Me_6)Ru(PMe_3)(OC(O)NHPh)(Ph) (**7**)

Charging a sealable NMR tube with ~30 mg of **3** in C_6D_6 with an atmosphere of carbon dioxide afforded a maximum 57% yield of insertion product, **7**, leaving the remaining **3** unchanged. Vigorous bubbling of carbon dioxide through solutions of **3** (0.100 g, 0.197 mmol) in 25 ml of either toluene or diethyl ether for 0.5 h, followed by removal of the solvent under reduced pressure resulted in 70% and 43% respective yields of **7**.

Reaction of **4** *with carbon dioxide. Synthesis of* (η^6-C_6Me_6)Ru(PMe_3)(OC(O)NHPh)(Me) (**8**)

Vigorous bubbling of carbon dioxide through a stirring solution of **5** (0.551 g, 1.234 mmol) in 40 ml of diethyl ether for 0.5 h caused a color change from bright red to pale red-yellow. The solution was left stirring under an atmosphere of carbon dioxide for an additional 0.5 h, during which time a yellow precipitate formed. Removal of the solvent under reduced pressure resulted in a quantitative yield of product **8**. The reaction may also be carried out in a sealable NMR tube as described in the reaction of 3 with carbon dioxide to give 100% conversion to **8**. IR (KBr): 3301.7 cm^{-1} (ν_{N-H}); 1638.1 cm^{-1} ($\nu_{C=O}$). Anal. Calc. for $C_{23}H_{36}NO_2PRu$: C, 56.31; H, 7.40; N, 2.86. Found: C, 56.39; H, 7.44; N, 2.85.

Synthesis of (η^6-C_6Me_6)Ru(PMe_3)(OC(O)NHC_6H_4 CH_3)(Ph) (**9**)

Vigorous bubbling of carbon dioxide through a stirring solution of **5** (0.702 g, 1.343 mmol) in 50 ml of toluene for 20 min caused a color change from bright red to pale brown-yellow. The solution was left stirring under an atmosphere of carbon dioxide for an additional 0.5 h, during which time a drab green oil formed. Removal of the solvent under reduced pressure left the green oil which was extracted into diethyl ether until the extracts were colorless. The combined extracts were reduced in volume and cooled to -20°C giving a dark green powder of **9**. The reaction may also be carried out in a sealable NMR tube as described in the reaction of 3 with carbon dioxide to give 100% conversion to **9**. IR (KBr): 3281.8 cm^{-1} (ν_{N-H}); 1631.8 cm^{-1} ($\nu_{C=O}$). Anal. Calc. for $C_{29}H_{40}NO_2PRu$: C, 61.47; H, 7.12; N, 2.47. Found: C, 61.25; H, 7.18; N, 2.41.

Synthesis of (η^6-C_6Me_6)Ru(PMe_3)[(MeOOC) C=C (COOMe)(NHPh)](Me) (**10**)

To a stirring solution of **4** (0.109 g, 0.244 mmol) in 30 ml of THF two equivalents of DMAD (0.06 ml) were added. The color of the solution immediately changed from red to dark green. The solution was allowed to stir for 0.5 h, after which the solvent was removed under reduced pressure leaving a thick, dark green oil. The oil was washed with 15 ml of pentane to remove excess DMAD, and the product was then extracted into diethyl ether until extracts were colorless. The combined extracts were reduced in volume and cooled to -50°C giving dark green powder as the product **9** (0.046 g, 0.078 mmol) in 32% yield. When this reaction is carried out in a sealed NMR tube with 0.020 g of 5 and a 10% excess of DMAD the reaction is observed to go to completion with the excess of DMAD left unreacted. IR (KBr): 3311.4 cm^{-1} (ν_{N-H}); 1702.0 cm^{-1} ($\nu_{C=O}$). Anal. Calc. for $C_{28}H_{42}N$-O_4PRu: C, 57.13; H, 7.19; N, 2.38. Found: C, 57.03; H, 7.17; N, 2.41.

Synthesis of (η^6-C_6Me_6)Ru(PMe_3)(OC(O)OH) (Me)$\cdot$ H_2O (**11**)

Vigorous bubbling of carbon dioxide through a stirring solution of **6** (0.085 g, 0.185 mmol) in 40 ml of diethyl ether for 0.5 h caused a color change from bright red to pale yellow. The solution was left stirring under an atmosphere of carbon dioxide for an additional 0.5 h, during which time a pale yellow precipitate formed. The solvent was filtered off and the powder dried under reduced pressure to give 11 (0.058 g, 0.145 mmol) in 78% yield. IR (KBr): 1607.8 cm^{-1} ($\nu_{C=O}$). Anal. Calc. for $C_1H_{31}O_3PRu$: C, 47.10; H, 7.67. Found: C, 47.08; H, 7.35. Compound **11** can also be synthesized by bubbling CO_2 through a toluene solution of the hydroxide complex, **12** (*vide infra*).

Reaction of **6** *with water. Synthesis of* (η^6-C_6Me_6)Ru(PMe_3)(OH)(Me)$\cdot$xH_2O (**12**)

A stirring solution of 10 (0.065 g, 0.141 mmol) in 20 ml of diethyl ether was prepared. Fifteen ml (sixfold excess) of deionized, degassed water was syringed into the solution three times at twenty minute intervals to give 18 equivalents of water. After the last addition the solution was stirred for 1 h, during which time a color change from bright red to yellow-brown was observed. Removal of solvent under reduced pressure afforded a brown oil. 15 ml of pentane was added to this oil and stirred for 1 h, after which the yellow-brown pentane solution was filtered off leaving a yellow powder. Drying the powder under reduced pressure afforded 12 in undetermined yield. IR (KBr): 3220 cm^{-1} (ν_{O-H}, broad).

X-ray crystal structure of 3

Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing MoK_α radiation ($\lambda = 0.71069$ Å). 50 reflections with $20.0^\circ \leqslant 2\theta \leqslant 22.0^\circ$ were used to refine the cell parameters. 9211 reflections (two equivalent sets) were collected using the ω-scan method (1.2° scan range and 3–6° scan speed depending on intensity). Four reflections were measured ever 96 reflections to monitor instrument and crystal stability (maximum correction on **I** was $<1\%$). Absorption corrections were not applied based because of the crystal shape and small size.

The structure was solved by the heavy-atom method in SHELXTL plus [7] from which the locations of the Ru atom was obtained. All of the non-H atoms were located from a subsequent Difference Fourier map. The structure was refined in SHELXTL plus using full-matrix least squares. The non-H atoms were treated anisotropically. The H-atoms on C21 were calculated in idealized positions and the thermal parameter of H21c was fixed at 0.08. The rest of the H-atoms were obtained from a subsequent Difference Fourier map and were refined without any constraints, except H6′b and the H-atoms on C1′ which have their thermal parameters fixed at 0.08. 409 parameters were refined and $\Sigma w\ (|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\ k\mathbf{I}^{-1/2}\ \{[\sigma(\mathbf{I})]^2 + (0.02\mathbf{I})^2\}^{1/2}$, $\mathbf{I}$(intensity) $= (\mathbf{I}_{\text{peak}} - \mathbf{I}_{\text{background}})$(scan rate), and $\sigma(\mathbf{I}) = (\mathbf{I}_{\text{peak}} + \mathbf{I}_{\text{background}})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography* [8]. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann [9] with anomalous-dispersion corrections from Cromer and Liberman [10], while those of hydrogen atoms were from Stewart *et al.* [11].

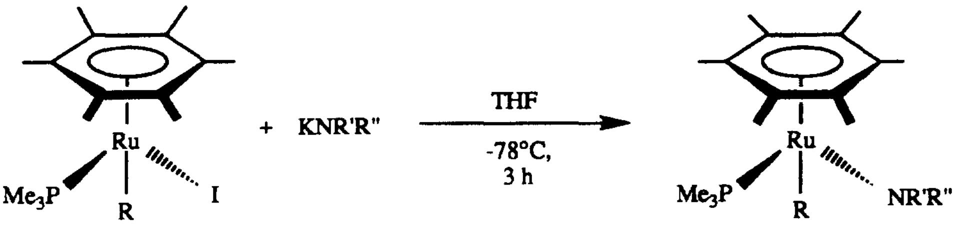
RESULTS AND DISCUSSION

We have found that reaction of KNR′R″ with (η^6-C_6Me_6)Ru(PMe_3)(R)I in THF proceeds rapidly to give good to moderate yields of the corresponding anilide complexes as shown in eqn (1).

In our experience, the success of the synthesis of anilide complexes via nucleophilic displacement of leaving groups from η^6-arene complexes of ruthenium is dependent upon the nature of the leaving group and the nature of the metal associated with the anilide anion. The chemistry in eqn (1) works most efficiently when I^- is the leaving group and K^+ is the anilide counterion. This chemistry stands in contrast to earlier results from this laboratory [1g] which showed that the reaction between (η^6-C_6Me_6)Ru(PMe_3)Cl_2 and LiNHPh proceeds via a complicated mechanism involving the loss of PMe_3 to give the bimetallic complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}NHPh)_3]^+$ as the anilide containing product. The presence of both the I^- and the R group in the starting material leads to cleaner and more predictable chemistry.

Compounds **3**–**6** are red, crystalline solids that are thermally stable, but air and moisture sensitive in solution and the solid state. They are soluble in ethereal solvents and aromatic hydrocarbons, and have been characterized via ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The NMR data for all the compounds reported are found in Tables 1–3. The ^{1}H NMR spectra typically display a single peak arising from the C_6Me_6 group as well as a doublet from the coordinated PMe_3 group. The methyl group in compounds **4** and **6** is responsible for a doublet at −0.13 and 0.40 ppm, respectively. There are a series of doublets and triplets in the aromatic region of the spectra that are due to the phenyl groups of the anilide or the Ru phenyl groups.

The NMR spectra of compound **6** are more complicated than those of **3**–**5** since more aromatic peaks are observed than can be accounted for if there is free rotation of the phenyl group in both the ^{1}H and ^{13}C spectra. In ^{13}C NMR spectrum of **6**, six peaks assignable to the aromatic carbons of **6** are observed. This observation is consistent with slow rotation of the



3; R=Ph, R′=H, R″=Ph
4; R=Me, R′=H, R″=Ph
5; R=Ph, R′=H, R″=*p*-tol
6; R=Me, R′=Me, R″=Ph

(1)

Table 1. ^{1}H NMR data[a]

Compound	δ ppm	Mult.	J. Hz	Integ.	Assignt.
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(Ph)I (**1**)[b]	1.19	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.67	s		18	$-C_6(C\underline{H}_3)_6$
	7.03	m		4	aromatic
	8.59	m, br		1	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(Me)I (**2**)[b]	0.75	d	$J^3_{\text{P-H}} = 11$	3	$-\underline{Me}$
	1.17	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.72	s		18	$-C_6(C\underline{H}_3)_6$
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(NHPh)Ph (**3**)[b]	0.86	d	$J^2_{\text{P-H}} = 8.5$	9	$-P\underline{Me}_3$
	1.34	s, br		1	$-N\underline{H}Ph$
	1.64	s		18	$-C_6(C\underline{H}_3)_6$
	6.41	m, br		3	aromatic
	7.13	m, br		+slvt	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(NHPh)Me (**4**)[d]	−0.13	d	$J^3_{\text{P-H}} = 9$	3	$-\underline{Me}$
	0.81	s, br		1	$-N\underline{H}Ph$
	1.13	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.95	s		18	$-C_6(C\underline{H}_3)_6$
	5.76	t of t		1	aromatic
	6.01	d, br		2	aromatic
	6.66	t, br		2	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(NHC$_6$H$_4$CH$_3$)Ph (**5**)[d]	0.91	s, br		1	$N\underline{H}C_6H_4Me$
	1.08	d	$J^2_{\text{P-H}} = 6$	9	$-P\underline{Me}_3$
	1.94	s		18	$-C_6(C\underline{H}_3)_6$
	2.06	s		3	$NHC_6H_4\underline{Me}$
	6.05	d		2	aromatic
	6.55	d		2	aromatic
	6.85	t		1	aromatic
	7.00	t, br		2	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(NMePh)Me (**6**)[b]	0.40	d	$J^3_{\text{P-H}} = 9$	3	$-\underline{Me}$
	0.85	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.61	s		18	$-C_6(C\underline{H}_3)_6$
	2.84	s		3	$-N\underline{Me}Ph$
	6.51	t		1	aromatic
	6.67	m, br		2	aromatic
	7.25	t		1	aromatic
	7.38	t		1	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(OC(O)NHPh)Ph (**7**)[b]	1.08	d	$J^2_{\text{P-H}} = 8.5$	9	$-P\underline{Me}_3$
	1.70	s		18	$-C_6(C\underline{H}_3)_6$
	6.38	d		1	aromatic
	6.60	s, br		1	$-OCON\underline{H}Ph$
	7.09	m, br		+slvt	aromatic
	7.56	d		2	aromatic
	8.16	d		1	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(OC(O)NHPh)Me (**8**)[d]	0.32	d	$J^3_{\text{P-H}} = 6$	3	$-\underline{Me}$
	1.26	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.95	s		18	$-C_6(C\underline{H}_3)_6$
	6.38	s, br		1	$-OCON\underline{H}Ph$
	6.76	t		1	aromatic
	7.13	t		2	aromatic
	7.29	d		2	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)[(MeOOC)C=C(COOMe)(NHPh)](Me) (**9**)[c]	−0.26	d	$J^3_{\text{P-H}} = 9$	3	$-\underline{Me}$
	1.18	d	$J^2_{\text{P-H}} = 9$	9	$-P\underline{Me}_3$
	1.96	s		18	$-C_6(C\underline{H}_3)_6$
	3.57	s		3	$-OC\underline{H}_3$
	3.59	s		3	$-OC\underline{H}_3$
	5.93	s, br		1	$-dmadN\underline{H}Ph$
	6.60	d		2	aromatic
	6.71	t		1	aromatic
	7.12	t		2	aromatic

Table 1—*Continued.*

Compound	δ ppm	Mult.	J. Hz	Integ.	Assignt.
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(OC(O)NHC$_6$H$_4$CH$_3$)Ph (**10**)[b]	1.06	d	$J^2_{\text{P-H}} = 9$	9	-P$\underline{\text{Me}}_3$
	1.69	s		18	-C$_6$(C$\underline{\text{H}}_3$)$_6$
	2.11	s		3	NHC$_6$H$_4\underline{\text{Me}}$
	6.63	s, br		1	N$\underline{\text{H}}$C$_6$H$_4$Me
	7.00	d		2	aromatic
	7.11	m, br		+slvt	aromatic
	7.44	m, br		3	aromatic
	8.13	m, br		1	aromatic
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(OC(O)OH)Me·H$_2$O (**11**)[c]	0.33	d	$J^3_{\text{P-H}} = 9$	3	-$\underline{\text{Me}}$
	1.22	d	$J^2_{\text{P-H}} = 9$	9	-P$\underline{\text{Me}}_3$
	1.91	s		18	-C$_6$(C$\underline{\text{H}}_3$)$_6$
	11.08	s, br		1	-OCO$_2\underline{\text{H}}$
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(OH)Me·xH$_2$O (**12**)[b]	−4.40	s, br		1	-O$\underline{\text{H}}$
	0.38	d	$J^3_{\text{P-H}} = 9$	3	-$\underline{\text{Me}}$
	1.04	d	$J^2_{\text{P-H}} = 9$	9	-P$\underline{\text{Me}}_3$
	1.75	s		18	-C$_6$(C$\underline{\text{H}}_3$)$_6$
	3.99	s, br			-x$\underline{\text{H}}_2$O

[a] All spectroscopic data were collected at 23°C. The multiplicity doublet is apparent splitting patterns when refering to the PMe$_3$ ligands and do not necessarily reflect the true coupling constants.

[b] C$_6$D$_6$.

[c] CDCl$_3$.

[d] CD$_2$Cl$_2$.

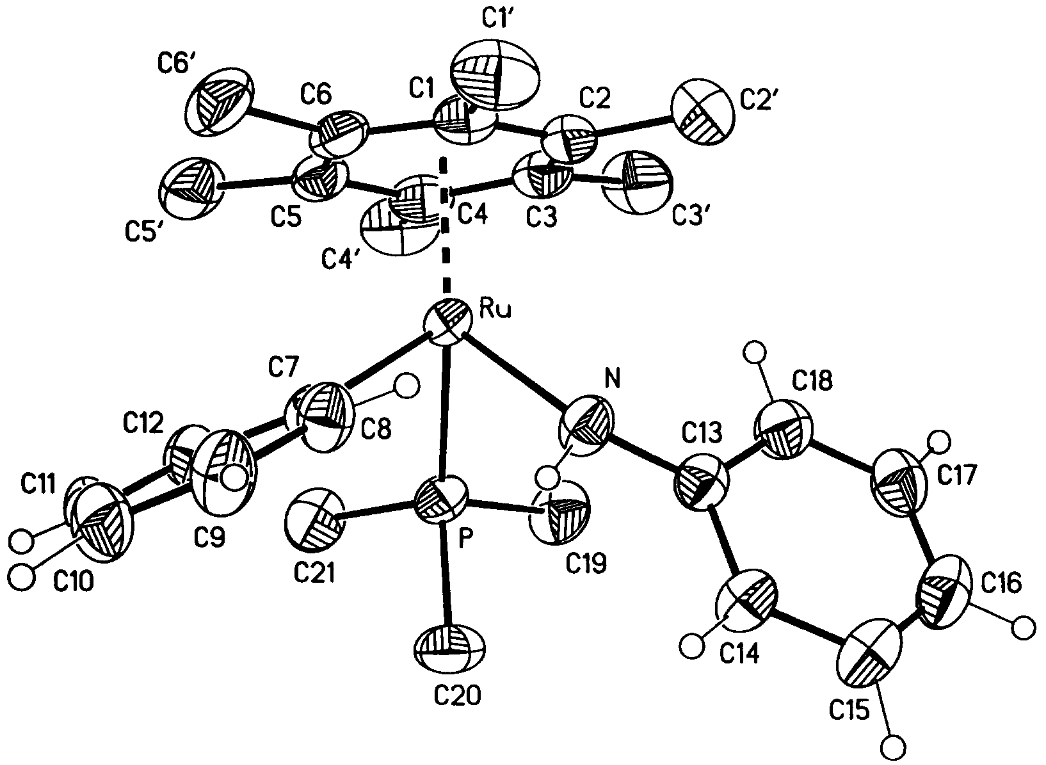


Fig. 1. Thermal ellipsoid plot of compound **3**.

Table 2. $^{13}C\{^1H\}$ NMR data[a]

Compound	δ ppm	Mult.	J. Hz	Assignt.
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(Ph)I$ (**1**)[c]	16.6	s		$-C_6(\underline{C}H_3)_6$
	19.2	d	$J^1_{P\text{-}C} = 32$	$-P\underline{Me}_3$
	98.0	d	$J^2_{P\text{-}C} = 3$	$-\underline{C}_6(CH_3)_6$
	121.0	s		aromatic
	125.7	s		aromatic
	127.0	s		aromatic
	140.2	d	$J^2_{P\text{-}C} = 15$	*ipso*-C
	147.1	s		aromatic
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(Me)I$ (**2**)[b]	−6.3	d	$J^2_{P\text{-}C} = 20$	$-\underline{Me}$
	16.3	s		$-C_6(\underline{C}H_3)_6$
	18.6	d	$J^1_{P\text{-}C} = 31$	$-P\underline{Me}_3$
	95.7	d	$J^2_{P\text{-}C} = 3$	$-\underline{C}_6(CH_3)_6$
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHPh)Ph$ (**3**)[b]	15.6	s		$-C_6(\underline{C}H_3)_6$
	16.7	d	$J^1_{P\text{-}C} = 28$	$-P\underline{Me}_3$
	98.9	d	$J^2_{P\text{-}C} = 3.6$	$-\underline{C}_6(CH_3)_6$
	108.9	s		aromatic
	117.1	s, br		aromatic
	121.4	s		aromatic
	128.3	s		aromatic
	161.5	s		aromatic
	170.2	d	$J^2_{P\text{-}C} = 22$	Ru-*ipso*-C
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHPh)Me$ (**4**)[b]	1.89	d	$J^2_{P\text{-}C} = 20$	$-\underline{Me}$
	15.3	s		$-C_6(\underline{C}H_3)_6$
	15.7	d	$J^1_{P\text{-}C} = 28$	$-P\underline{Me}_3$
	96.6	d	$J^2_{P\text{-}C} = 3.8$	$-\underline{C}_6(CH_3)_6$
	107.6	s		aromatic
	108.9	s		aromatic
	128.6	s		aromatic
	162.1	d	$J^3_{P\text{-}C} = 2.5$	*ipso*-C
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHC_6H_4CH_3)Ph$ (**5**)[d]	16.2	s	$-C_6(\underline{C}H_3)_6$	
	17.2	d	$J^1_{P\text{-}C} = 28$	$-P\underline{Me}_3$
	20.1	s		$NHPh\text{-}\underline{CH_3}$
	99.6	d	$J^2_{P\text{-}C} = 3.8$	$-\underline{C}_6(CH_3)_6$
	116.1	s		aromatic
	116.9	s, br		aromatic
	121.1	s		aromatic
	128.9	s		aromatic
	140.5	s		aromatic
	159.6	d		aromatic
	170.8	d	$J^2_{P\text{-}C} = 22$	Ru-*ipso*-C
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NMePh)Me$ (**6**)[b]	2.61	d	$J^2_{P\text{-}C} = 22$	$Ru\text{-}\underline{Me}$
	15.6	s		$-C_6(\underline{C}H_3)_6$
	16.0	d	$J^1_{P\text{-}C} = 28$	$-P\underline{Me}_3$
	42.0	s		$-N\underline{Me}Ph$
	97.0	d	$J^2_{P\text{-}C} = 3$	$-\underline{C}_6(CH_3)_6$
	107.6	s		aromatic
	111.7	s		aromatic
	121.3	s		aromatic
	127.0	s		aromatic
	129.5	s		aromatic
	161.7	d	mom0]1.71	*ipso*-C
			$J^3_{P\text{-}C} = 1.5$	
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OC(O)NHPh)Me$ (**8**)[d]	1.87	d	$J^2_{P\text{-}C} = 20$	$Ru\text{-}\underline{Me}$
	15.4	d	$J^1_{P\text{-}C} = 28$	$-P\underline{Me}_3$
	15.7	s		$-C_6(\underline{C}H_3)_6$
	95.7	d	$J^2_{P\text{-}C} = 3.3$	$-\underline{C}_6(CH_3)_6$
	117.1	s		aromatic
	120.0	s		aromatic
	128.7	s		aroamtic
	142.9	s		carbonyl
	159.8	d	$J^5_{P\text{-}C} = 4.3$	*ipso*-C

Table 2—*Continued.*

Compound	δ ppm	Mult.	J. Hz	Assignt.
(η^6-C_6Me_6)Ru(PMe_3)[(MeOOC)C=C(COOMe)(NHPh)](Me) (**9**)[c]	−1.71	d	$J^2_{P-C} = 19$	$Ru-\underline{Me}$
	15.9	s		$-C_6(\underline{C}H_3)_6$
	17.4	d	$J^1_{P-C} = 30$	$-P\underline{Me}_3$
	49.2	s		methoxy C
	51.3	s		methoxy C
	99.2	d	$J^2_{P-C} = 3.2$	$-\underline{C}_6(CH_3)_6$
	115.7	s		aromatic
	118.6	s		aromatic
	128.8	s		aromatic
	132.4	d	$J^3_{P C} = 4.6$	$Ru-C=\underline{C}$
	145.7	s		*ipso*-C
	162.7	d	$J^2_{P-C} = 17$	$Ru-\underline{C}=C$
	163.5	d	$J^3_{P C} = 1.6$	$Ru-C-\underline{C}=O$
	176.2	s		$-C=C-\underline{C}=O$
(η^6-C_6Me_6)Ru(PMe_3)(OC(O)NH$C_6H_4CH_3$)Ph (**10**)[b]	15.7	s		$-C_6(\underline{C}H_3)_6$
	15.9	d	$J^1_{P C} = 29$	$-P\underline{Me}_3$
	20.7	s		$NHPh-\underline{C}H_3$
	97.7	d	$J^2_{P-C} = 2.3$	$-\underline{C}_6(CH_3)_6$
	117.8	s		aromatic
	121.9	s, br		aromatic
	126.0	s		aromatic
	127.0	s		aromatic
	129.3	s		aromatic
	136.4	s		aromatic
	139.9	s		aromatic
	140.6	d		carbonyl
	160.2	s		aromatic
	167.8	d	$J^2_{P-C} = 24$	Ru-*ipso*-C
(η^6-C_6Me_6)Ru(PMe_3)(OC(O)OH)Me·H_2O (**11**)[c]	2.07	d	$J^2_{P-C} = 20$	$Ru-\underline{Me}$
	15.1	d	$J^1_{P-C} = 28.5$	$-P\underline{Me}_3$
	15.4	s		$-C_6(\underline{C}H_3)_6$
	95.2	d	$J^2_{P C} = 3$	$-\underline{C}_6(CH_3)_6$
	161.8	s		carbonyl
(η^6-C_6Me_6)Ru(PMe_3)(OH)Me·xH_2O (**12**)[b]	1.24	d	$J^2_{P-C} = 20$	$Ru-\underline{Me}$
	14.6	d	$J^1_{P-C} = 27$	$-P\underline{Me}_3$
	15.3	s		$-C_6(\underline{C}H_3)_6$
	95.0	d	$J^2_{P-C} = 3$	$-\underline{C}_6(CH_3)_6$

[a] All spectroscopic data were collected at 23°C. The multiplicity doublet is apparent splitting patterns when referring to the PMe_3 ligands and do not necessarily reflect the true coupling constants.

[b] C_6D_6.

[c] $CDCl_3$.

[d] CD_2Cl_2.

phenyl group on the NMR timescale and probably arises from steric interactions between the MeNPh group and the rest of the molecule. Hindered rotation about P—Ph and Rh—Ph groups has been observed in the isoelectronic, and closely related compounds, Cp*Rh(Ph)(X)(PR_3) [6]. Though we have not investigated the low temperature NMR behavior of compounds **3**–**5**, observable barriers to rotation about the Ru—Ph and N—Ph bonds might be expected by analogy with the Rh compounds.

Crystals of **3** suitable for a single crystal X-ray diffraction study were grown by slowly cooling a saturated Et_2O solution of **3** to −40°C. A thermal ellipsoid plot of **3** is shown in Fig. 1, while data collection parameters and selected bond lengths and angles are found in Tables 4 and 5. The compound has the expected three legged piano stool geometry with the PMe_3, NHPh, and Ph groups defining the "legs" of the piano stool. The angles between these groups are slightly less than 90° and suggest a significant steric influence from the C_6Me_6 group as is consistent with the observed hindered rotation of the phenyl groups in NMR spectra of **6**. The geometry about the nitrogen atom of the anilide is planar as is typically observed

Table 3. $^{31}P\{^1H\}$ NMR data[a]

Compound	δ ppm	mult.
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(Ph)I$ (**1**)[c]	38.32	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(Me)I$ (**2**)[c]	2.68	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHPh)Ph$ (**3**)[b]	5.27	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OC(O)NHPh)Ph$ (**4**)[b]	5.92	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHPh)Me$ (**5**)[b]	9.58	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OC(O)NHPh)Me$ (**6**)[b]	48.16	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)[(MeOOC)C{=}C(COOME)(NHPh)](Me)$ (**7**)[b]	44.04	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NHC_6H_4CH_3)Ph$ (**8**)[d]	46.05	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OC(O)NHC_6H_4CH_3)Ph$ (**9**)[b]	5.84	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(NMePh)Me$ (**10**)[b]	9.10	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OC(O)OH)Me \cdot H_2O$ (**11**)[c]	10.21	s
$(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(OH)Me \cdot xH_2O$ (**12**)[b]	8.16	s

[a] All spectroscopic data were collected at 23°C.

[b] C_6D_6.

[c] $CDCl_3$.

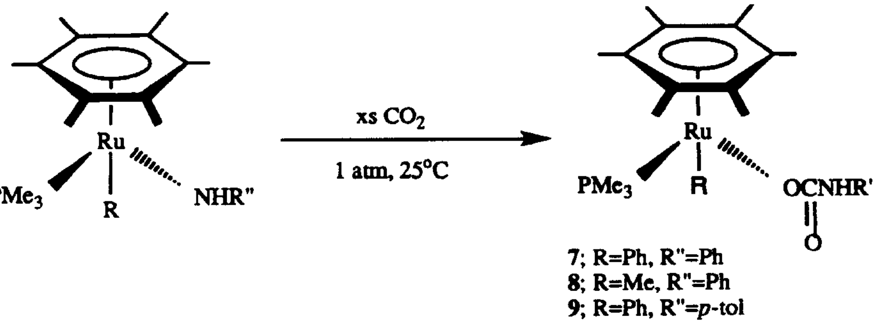
[d] CD_2Cl_2.

in transition metal amide complexes even when the metal center is electronically saturated as in groups 8–10. The Ru—N—C(13) angle of 135° is also indicative of the steric congestion in the coordination sphere.

The bond lengths are generally unremarkable with the exception of the rather short distance of 1.360(5) between C13 and N in the anilide group. Shortened C—N bonds in other anilides of late transition metal complexes have been observed previously, and are consistent with some amount of stabilization of the nitrogen lone pair through π interaction with the phenyl ring [12]. Given the electronic saturation of the metal center in these complexes, π donation from the N to the metal is not possible, and interaction between the phenyl ring and the amide N may help to stabilize the complex.

We have explored the reactivity of compounds **3**–**6** with the unsaturated electrophiles CO_2 and DMAD. The reaction between CO_2 and compounds **3**–**5** results in the net insertion of the CO_2 into the Ru—N bond to give a metal carbamate complex as is shown in eqn (2). Given the electronic saturation at the metal centre, it is likely that these reactions occur via direct attack of the N lone pair on CO_2 followed by Ru—O bond formation. This type of reactivity is well precedented in other group 8–10 metal amido complexes [13]. Interestingly, the complexes display a range of reactivity with CO_2. When the reaction between **3** and excess CO_2 was monitored by ^1H NMR spectroscopy, the reaction proceeded to only 70% conversion, while the same reaction with **4** or **5** resulted in quantitative conversion to products. It would appear that the increased electron richness of the *p*-toluamide ligand in **5** and the better electron donating Me group in **4** (vs the Ph group in **3**) make the N atom more nucleophilic in **4** and **5** which allows the reaction to go to completion.

The differences in the reactivity of **3**–**5** are more obvious when these compounds are allowed to react with DMAD. Thus, while the anilide and *p*-toluamide complexes, **3** and **5** do not react with DMAD, complex **4** reacts to give a quantitative yield of the insertion product, **9**, eqn (3). It would appear that this difference in reactivity is due to the increased electron donating ability of the Me group of **4** relative to the Ph groups of **3** and **5** and is consistent with the reac-



(2)

Table 4. Crystallographic data

A. Crystal data (298 K)	**3**
a (Å)	12.013(2)
b (Å)	16.700(3)
c (Å)	12.414(1)
β (°)	97.35(2)
V (Å^3)	2470.0(7)
$d$calc (g cm^{-3}) (298 K)	1.37
Empirical formula	$C_{27}H_{38}NPRu$
Formula wt, g	508.6
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
F(000) electrons	1064
B. Data collection (298 K)	
Radiation λ (Å)	Mo–K_α, 0.71073
Mode	ω-scan
Scan range	Symmetrically over 1.2 about $K_{\alpha1,2}$ maximum
Background	offset 1.0 and −1.0 in ω from $K_{\alpha1,2}$ maximum
Scan rate (°) min^{-1}	3–6
2θ range (°)	3–50
Range of h k l	$0 \leqslant h \leqslant 14$
(2 equivalent sets)	$-19 \leqslant k \leqslant 19$
	$-14 \leqslant l \leqslant 14$
Total reflections measured	9211 (two equivalent sets)
Unique reflections	4356
Absorption coeff. μ (Mo–K_α), cm^{-1}	7.13
C. Structure refinement	
S, Goodness-of-fit	1.08
Reflections used, $I > 2\sigma(I)$	3174
No. of variables	409
R, wR* (%)	2.74, 3.18
R, wR*, all data (%)	4.95, 3.96
$R_{int.}$ (%)	1.54
Max. shift/esd	0.001
Min. peak in diff. four. map (e Å^{-3})	−0.32
Max. peak in diff. four. map (e Å^{-3})	0.43

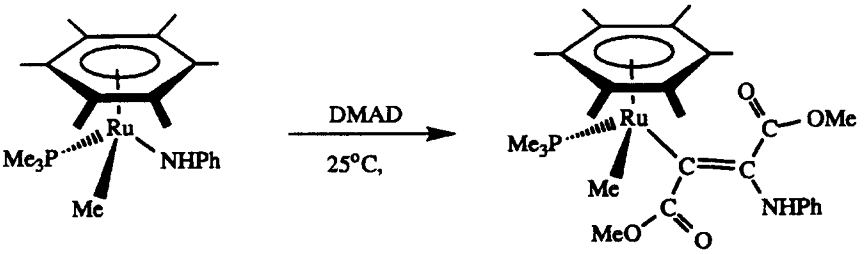
* Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes.

Function minimized was $w(|F_o|-|F_c|)^2$, where $w=(\sigma(F))^{-2}$

$R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

$wR=[\Sigma w(|F_o|-|F_o|)^2/\Sigma/F_o|^2]^{1/2}$

$S=[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$.



4

10

(3)

Table 5. Bond lengths (Å) and angles (°) for compound 3

1	2	3	1–2 (Å)	1–2–3(°)
P	Ru	N	2.2919(9)	84.76(9)
N	Ru	C7	2.121(3)	84.18(12)
C7	Ru	P	2.096(3)	86.55(9)
C13	N	Ru	1.360(5)	135.4(2)
C1	Ru		2.263(4)	
C2	Ru		2.301(4)	
C3	Ru		2.329(4)	
C4	Ru		2.228(4)	
C5	Ru		2.241(3)	
C6	Ru		2.268(3)	

tivity of these compounds with CO_2. Unfortunately, we cannot rule out the possibility that the observed differences in reactivity with DMAD are due to the difference in the steric effects of the Ru—Me and Ru—Ph groups.

The *N*-methyl anilide complex, **6**, is considerably more reactive than **3**–**5**. Instead of reacting with CO_2 to give the expected carbamate complex, the product of the reaction between **6** and CO_2 is the bicarbonate complex, $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(HCO_3)$, **11**. We believe that the conversion of **6** to **11** involves traces of H_2O in the CO_2 which either converts **11** to a hydroxide, **12**, which reacts further with CO_2, or that the product carbamate complex reacts with H_2O giving **11** as the reaction product.

In order to test this hypothesis, complex **6** was converted to the hydroxide complex, **12** through its reaction with water. Compound **12** is isolated as a yellow powder that is soluble in ethereal solvents, and insoluble in aliphatic hydrocarbons. The ^1H NMR spectrum of **12** shows two broad peaks at -4.40 and 3.99 ppm respectively that might be assigned to the hydroxide proton. Given the variability of the integration of the peak at 3.99 ppm from sample to sample, we are inclined to assign the peak at -4.40 ppm to the hydroxide proton by analogy with $Cp^*Ir(PMe_3)Ph(OH)^{2a}$, and the peak at 3.99 ppm to the water of hydration [14]. When **12** is allowed to react with CO_2, it is rapidly and quantitatively converted into the bicarbonate complex, **11** as shown in eqn (4). The nucleophilicity of the hydroxide group in **12** is expected and the reaction between other late transition metal hydroxides and unsaturated electrophiles is well precedented [2a,15].

Preliminary studies indicate that compound **12** does not react with ethylene at low to elevated temperatures and 1 atm pressure. This lack of reactivity differs from the related complex $Cp^*Ir(OH)(Me)(PMe_3)$, which has been shown to react with ethylene via a complicated mechanism with the net result being insertion of the ethylene into the Ir—O bond [2]. We are continuing to investigate the reactivity of **12** with a variety of substrates.

In summary, the synthesis of a series of anilide complexes of the type, $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)(R)NR'Ph$, can be achieved via nucleophilic displacement of iodide from the corresponding precursor complexes using potassium anilides. Unsaturated electrophiles react with the anilide complexes by attacking the lone pair of the anilide nitrogen and resulting in net insertion of the electrophile into the Ru N bond. The nucleophilicity of the N (or in the case of **12**, O) atom of these complexes is likely due to the fact that the Ru atom in these 18 e^- complexes cannot function as a π acceptor toward the anilide or hydroxide donors.

SUPPLEMENTARY MATERIAL AVAILABLE

Positional parameters, and a complete listing of bond lengths and angles.

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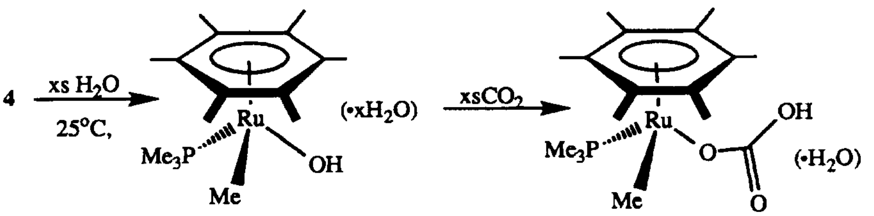

12 **11** (4)

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