Organometallics **2009,** *28,* 567–572

Stable Cationic and Neutral Ruthenabenzenes

George R. Clark, Tamsin R. O'Neale, Warren R. Roper,* Deborah M. Tonei, and
L. James Wright*

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

Received September 4, 2008

Reversible protonation of the purple ruthenabenzofuran (or tethered ruthenacyclohexadiene) Ru[C_5H_2-(CO_2Me-2)(CO_2Me-4)($CHCO_2Me$-5)](CO)(PPh_3)$_2$ (**1**) with $HBF_4 \cdot OEt_2$ gives the structurally characterized stable cationic tethered ruthenabenzene [Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)(CH_2CO_2Me-5)](CO)(PPh_3)$_2$]-[(BF_4)$_2$H] (**2**), while the thermal reaction of **1** with HCl forms the stable neutral tethered ruthenabenzene Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)(CH_2CO_2Me-5)]Cl(PPh_3)$_2$ (**3**) as the major product. The cyclopentadienyl complex Ru(η^5-C_5H_2(CH_2CO_2Me-1)(CO_2Me-2)(CO_2Me-4)Cl(CO)(PPh_3) (**4**), which is formed in this reaction as a minor product, can be separated from **3** by chromatography. Treatment of the ruthenabenzene **3** with CNR (R = *p*-tolyl) gives the purple ruthenabenzofuran (or tethered ruthenacyclohexadiene) complex Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)($CHCO_2Me$-5)](CNR)(PPh_3)$_2$ (**5**), which is the isocyanide analogue of **1**.

Introduction

Metallabenzenes are now a well-established class of organometallic compounds, and considerable attention has been directed toward developing synthetic routes and studying the reaction chemistry of these compounds.[1] In addition, important fundamental information has been provided by a number of computational studies that have explored aspects of the syntheses, reactivity, decomposition pathways, and aromatic character of these materials.[1,2] Despite this scrutiny, nearly all of the reported metallabenzenes that are stable under ambient conditions are confined to derivatives of the third-row transition metals osmium, iridium, and platinum. Metallabenzenes or metallabenzenoids of the first- or second-row transition metals iron,[3] chromium,[4] and ruthenium[5,6] have been proposed as reactive intermediates, and the ruthenabenzene Ru[C(Ph)CH-CHC(Ph)C(OEt)](CO)Cp, a related ruthenaphenoxide, and a ruthenaphenanthrene oxide have been detected spectroscopically at low temperatures.[6] However, it was not until 2006 that the first stable metallabenzene of a second-row transition metal was isolated. In that year Jia, Xia, and co-workers reported the synthesis and study of the ruthenabenzene [Ru[CHC(PPh_3)-CHC(PPh_3)CH]Cl_2(PPh_3)$_2$]Cl.[7] This remarkable compound remains mostly unchanged after heating in the solid state in air at 100 °C for 5 h. It was proposed that the two bulky triphenylphosphonium substituents on the ruthenabenzene ring play an important role in stabilizing this compound as well as the other related ruthenabenzene derivatives that were subsequently obtained by ligand substitution at ruthenium.[8] These compounds remain the only simple metallabenzenes that involve a metal from the second transition series that are stable under ambient conditions.

In this paper we now report (i) the synthesis of the stable blue cationic tethered ruthenabenzene [Ru[C_5H_2(CO_2Me-2)-(CO_2Me-4)(CH_2CO_2Me-5)](CO)(PPh_3)$_2$][(BF_4)$_2$H] (**2**) through protonation of the ruthenabenzofuran (or tethered ruthenacyclohexadiene) Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)($CHCO_2Me$-5)](CO)(PPh_3)$_2$ (**1**) with $HBF_4 \cdot OEt_2$; (ii) the synthesis of the stable green neutral tethered ruthenabenzene Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)(CH_2CO_2-Me-5)]Cl(PPh_3)$_2$ (**3**) through reaction of **1** with HCl in benzene/methanol solution heated under reflux; (iii) isolation of the cyclopentadienyl complex Ru(η^5-C_5H_2(CH_2CO_2Me-1)(CO_2Me-2)(CO_2Me-4)Cl(CO)(PPh_3) (**4**) as a byproduct from the thermal reaction of **1** with HCl; (iv) the conversion of **3** to the ruthenabenzofuran (or tethered ruthenacyclohexadiene) complex Ru[C_5H_2-(CO_2Me-2)(CO_2Me-4)($CHCO_2Me$-5)](CNR)(PPh_3)$_2$ (**5**) through treatment with *p*-tolylisocyanide, and (v) the crystal structures of **2**, **4**, and **5**.

Results and Discussion

In a recent paper we described the synthesis and some reaction chemistry of the osmabenzofuran Os[C_7H_2O(OMe-7)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$.[9] The case for considering this compound as an osmabenzofuran with delocalized bonding was developed on the basis of spectroscopic, structural, and reactivity data. One of the important reactions this compound undergoes is protonation of C6 in the osmafuran ring to form the cationic, tethered osmabenzene [Os[C_5H(CH_2CO_2Me-5)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$]$^+$ (see Chart 1).[9] A ruthenium complex, Ru[C_5H_2(CO_2Me-2)(CO_2Me-4)($CHCO_2Me$-5)](CO)(PPh_3)$_2$ (**1**), that has the same basic metallabicyclic skeleton as this osmabenzofuran and can also be considered as a ruthenabenzofuran[9] (see Chart 2 and discussion below) has been reported to form through reaction

---

* Corresponding authors. E-mail: lj.wright@auckland.ac.nz; w.roper@auckland.ac.nz.

[1] For example see: (a) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205. (b) Landorf, C. W.; Haley, M. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3914. (c) Wright, L. J. *J. Chem. Soc., Dalton Trans.* **2006**, 1821, and references therein.

[2] (a) Fernández, I.; Frenking, G. *Chem.–Eur. J.* **2007**, *13*, 5873. (b) Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2007**, *26*, 1986.

[3] Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463.

[4] Sivavec, T. M.; Katz, T. J. *Tetrahedron Lett.* **1985**, *26*, 2159.

[5] Yang, J.; Yin, J.; Abboud, K. A.; Jones, W. M. *Organometallics* **1994**, *13*, 971.

[6] Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 9776.

[7] Zhang, H.; Xia, H.; He, G.; Wen, T.; Gong, L.; Jia, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2920.

[8] Zhang, H.; Feng, L.; Gong, L.; Wu, L.; He, G.; Wen, T.; Yang, F.; Xia, H. *Organometallics* **2007**, *26*, 2705.

[9] Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2006**, *25*, 1771.

10.1021/om800857k CCC: $40.75

Chart 1

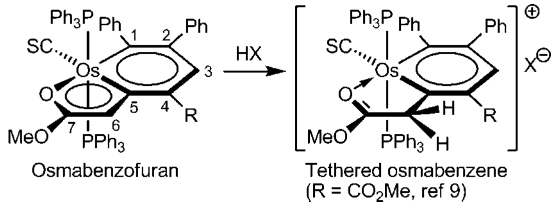
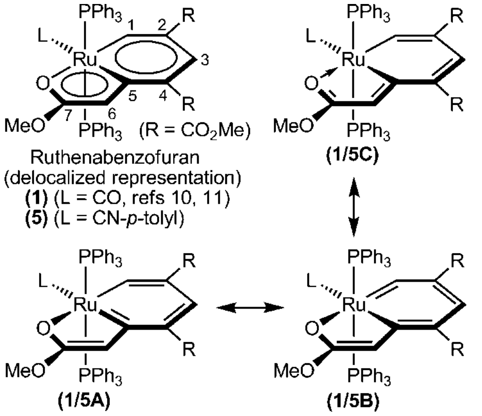


Chart 2

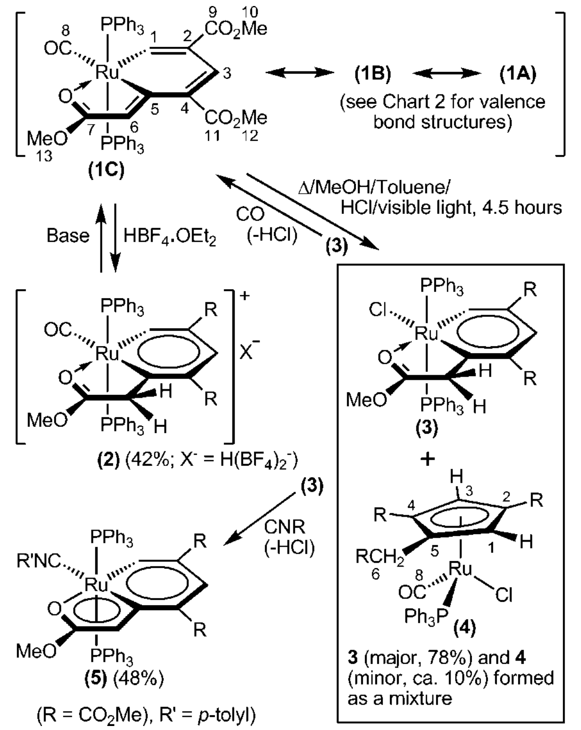


Valence bond structures **A**, **B** and **C** for **1** and **5**

between $RuH_2(CO)(PPh_3)_3$ and methyl propiolate.[10,11] We therefore investigated the reactions of **1** with acid to determine whether a related protonation reaction would occur at C6 in the ruthenafuran ring, thereby leading to the formation of a tethered ruthenabenzene.

On treatment of a toluene solution of purple $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CO)(PPh_3)_2$ (**1**) with $HBF_4 \cdot OEt_2$, the solution immediately turns dark blue, and dark blue crystals of the cationic, tethered ruthenabenzene $[Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)](CO)(PPh_3)_2][(BF_4)_2H]$ (**2**) are deposited from solution (see Scheme 1). Although **2** can be successfully recrystallized from dichloromethane/toluene, this protonation reaction is readily reversed, and addition of bases such as NEt_3 to dichloromethane solutions of this product causes immediate reversion back to **1**. Complex **2**, which is stable in solution at 25 °C for days, has been thoroughly characterized, including by a crystal structure determination (see below). Characterizing data for **2** as well as **3**−**5** are collected in the Experimental Section, and the numbering scheme used for the NMR assignments is given in Scheme 1. In the ^1H NMR spectrum of **2**, H1 appears as a doublet ($^4J_{H1H3}$ = 2.4 Hz) at 14.97 ppm. Resonances in this downfield region are typically observed for protons attached to the metal-bound carbon atoms of metallabenzenes,[1] and the signal for the two equivalent RuCH atoms in the stable ruthenabenzene $[Ru[CHC(PPh_3)CHC(PPh_3)CH]Cl_2(PPh_3)_2]Cl$ appears at 17.5 ppm.[7] H3 (8.83 ppm) in **2** appears in the aromatic region, and the two protons attached to C6 are observed at 2.73 ppm (cf. 6.06 ppm in **1**), consistent with saturation of this ring carbon atom. In the ^{13}C NMR spectrum of **2**, C1 and C5 appear as triplets at 290.8 ($^2J_{CP}$ = 6.1 Hz) and 283.6 ($^2J_{CP}$ = 7.7 Hz) ppm, respectively, positions that are very similar to that reported for the two equivalent RuC atoms in the ruthenabenzene $[Ru[CHC(PPh_3)CHC(PPh_3)CH]Cl_2(PPh_3)_2]Cl$ (284.3 ppm).[7] C6 is observed at 52.3 ppm (cf. 119 ppm in **1**), again consistent with saturation of this carbon atom.

Scheme 1. Synthesis of the Tethered Metallabenzenes 2 and 3 and Formation of the Ruthenabenzofuran 5



The crystal structure of complex **2** was determined, and the structure of the cationic ruthenium complex is shown in Figure 1 (crystal data for **2** as well as for **4** and **5** are given in the Supporting Information). The geometry about Ru is approximately octahedral, and the six atoms of the ruthenabenzene ring (Ru, C1−C5) and the three atoms of the tethering arm (C6, C7, and O6) are all essentially coplanar (maximum deviation from the mean plane through all nine atoms is 0.072 Å). The Ru−C1 and Ru−C5 distances are 1.933(4) and 2.045(5) Å, respectively. The *trans*-influence of the CO ligand is probably the main factor responsible for the greater length of the Ru−C5 bond. The C−C distances within the ruthenabenzene ring of **2** (C1−C2, 1.404(6); C2−C3, 1.383(7); C3−C4, 1.413(7); C4−C5,

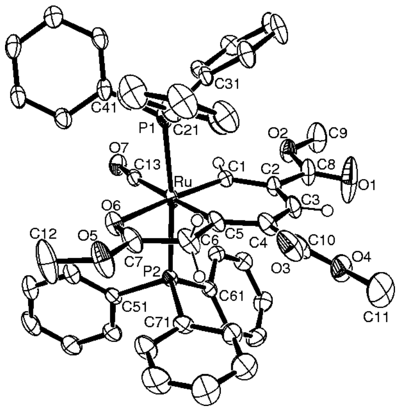


Figure 1. Molecular structure of the ruthenium cation of **2** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ru−C1 1.933(4), Ru−C5 2.045(5), Ru−C13 1.941(5), Ru−O6 2.216(3), C1−C2 1.404(6), C2−C3 1.383(7), C3−C4 1.413(7), C4−C5 1.374(7), C5−C6 1.518(7), C6−C7 1.504(8), O6−C7 1.231(7).

---

[10] Yamazaki, H.; Aoki, K. *J. Organomet. Chem.* **1976**, *122*, C54.

[11] Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **2000**, *53*, 99.

1.374(7) Å) are close to those found in benzene (1.390 Å)[12] and show relatively little alternation. The C5−C6 and C6−C7 distances (1.518(7) and 1.504(8) Å, respectively) in **2** are significantly longer than the corresponding distances in **1** (1.384(8) and 1.41(1) Å), consistent with saturation of C6. The counteranion in the crystal is comprised of the very unusual $[(BF_4)_2H]^-$ ion. The fluorine atoms in one of the $[BF_4]^-$ groups (the one involving B2) in this counteranion are disordered between two slightly different positions, and the half-weighted sets of atoms used in the refinement are labeled F5a−F8a and F5b−F8b. In each orientation of the disordered BF_4^- unit one fluorine atom (F8a or F8b) makes a close approach to F4 of the other ordered BF_4^- (B1) unit, with F4···F8a = 2.597 Å and F4···F8b = 2.750 Å. Both these distances are longer than the F−H···F distance of 2.49 Å in crystalline hydrogen fluoride,[13] but both are considerably shorter than the sum of the van der Waals radii for two fluorine atoms (ca. 2.94 Å)[14] and are therefore consistent with a hydrogen bond between F4 and F8a/b. Furthermore, the B1−F4 distance (1.428(10) Å) is longer than the other three B1−F distances (B1−F1, 1.361(9); B1−F2, 1.366(8); B1−F3, 1.379(9) Å), and likewise the B2−F8a and B2−F8b distances are longer than the other B2−F distances. In the difference Fourier map there is a peak between F4 and the disordered atoms F8a and F8b. However, the position of this peak was not sufficiently reliable to justify its inclusion as a hydrogen atom in the least-squares refinement. Although this putative hydrogen atom was not located in the crystal structure determination, its presence can be inferred from the structural features noted above. In the ^{19}F NMR spectrum of **2** only one sharp resonance at −154.49 ppm is observed, indicating that in solution equilibration of the positions of all fluorine atoms occurs rapidly on the NMR time scale.

In an attempt to prepare a neutral ruthenabenzene, the reaction of **1** with HCl was investigated. It was found that on heating **1** under reflux for 4.5 h in benzene/methanol that contains a small amount of trimethylsilyl chloride (a convenient way of introducing nonaqueous HCl to the system) while irradiating the mixture with visible light, the solution slowly changes color from purple to bright green. After purification of the reaction products by column chromatography two products were obtained, the green neutral ruthenabenzene $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)]Cl(PPh_3)_2$ (**3**), in 78% yield, and the yellow cyclopentadienyl complex $Ru(\eta^5\text{-}C_5H_2(CH_2CO_2Me\text{-}1)(CO_2Me\text{-}2)(CO_2Me\text{-}4)Cl(CO)(PPh_3)$ (**4**) in ca. 10% yield (see Scheme 1). The ruthenabenzene **3** is remarkably stable in solutions that contain traces of HCl, even at elevated temperatures, as is indicated by the synthetic procedure described above. We were not able to obtain the crystal structure of **3** because of the difficulty in obtaining single crystals suitable for X-ray diffraction studies; however, the spectroscopic and analytical data confirm the ruthenabenzene formulation. In the ^{1}H NMR spectrum of **3**, H1 appears as a doublet of triplets at 16.45 ppm ($^4J_{HH}$ = 2.7, $^3J_{HP}$ = 3.0 Hz), H3 is observed as a doublet at 8.76 ppm ($^4J_{HH}$ = 2.4 Hz), and the two protons on C6 appear as a singlet at 3.19 ppm. In the ^{13}C NMR spectrum the two metal-bound carbon atoms again appear as triplets at characteristically low field values (C1, 287.8 ($^2J_{CP}$ = 12.6 Hz); C5, 289.3 ($^2J_{CP}$ = 10.6 Hz) ppm), and the other ruthenabenzene ring carbon atoms have resonances in the aromatic region. The methylene carbon C6 is observed at 56.2 ppm, and in the ^{31}P NMR spectrum a singlet at 21.55 ppm is observed for the two equivalent phosphorus atoms.

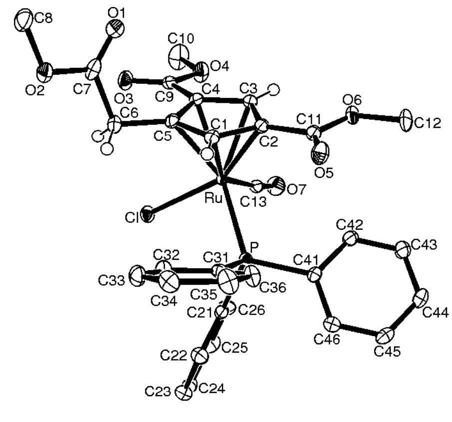


Figure 2. Molecular structure of **4** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ru−C13 1.8729(18), Ru−C1 2.2942(17), Ru−C2 2.2069(17), Ru−C3 2.1808(17), Ru−C4 2.2222(16), Ru−C5 2.3113(16), Ru−P 2.3260(4), Ru−Cl 2.3914(4), C5−C6 1.499(2), C6−C7 1.528(3).

The other product formed during the synthesis of **3** from **1** was the cyclopentadienyl complex $Ru(\eta^5\text{-}C_5H_2(CH_2CO_2Me\text{-}1)(CO_2Me\text{-}2)(CO_2Me\text{-}4)Cl(CO)(PPh_3)$ (**4**) (see Scheme 1). If the reaction conditions described above were changed so that the acid used was concentrated aqueous HCl and the solution was not irradiated with visible light, the ratio of **3** to **4** in the crude product was close to 1.0 (as estimated by NMR spectroscopy). We do not have any direct evidence relating to the mechanism by which **3** and **4** are formed from **1**, but a plausible sequence involves protonation of C6 in **1** followed either by (i) loss of CO from the resulting cationic intermediate and coordination of chloride to give **3** (irradiation with visible light could facilitate CO dissociation leading to increased yields of **3**) or (ii) the coupling of C1 and C5 in the cationic intermediate to give an η^1-cyclopentadienyl complex, which then rearranges with coordination of chloride to give the η^5-cyclopentadienyl complex **4**. There is ample evidence for the transformation of metallabenzenes into cyclopentadienyl complexes,[1] and this metallabenzene decomposition route has been studied by computational methods.[15]

The characterizing spectroscopic data relating to **4** are collected in the Experimental Section and are mostly unremarkable. In the ^{1}H NMR spectrum the two inequivalent protons on C6 are observed as doublets at 2.88 and 3.91 ppm, with geminal HH coupling constants of 17.8 Hz. In the ^{13}C NMR spectrum the saturated carbon atom C6 appears at 32.6 ppm. The crystal structure of **4** was determined, and the molecular structure is shown in Figure 2. The carbon atoms C2−4 of the π-bound cyclopentadienyl ligand make slightly closer approaches to ruthenium than C1 and C5. The atoms C6 and C7 that formed part of the five-membered ruthenacyclic ring in **1** are found within the CH_2CO_2Me substituent on the cyclopentadienyl ring in **4**.

Although the ruthenabenzene **3** is very stable in solutions that contain traces of HCl, addition of the base NEt_3 or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) results in the complete conversion of **3** to intractable mixtures of products. In contrast, treatment of a dichloromethane solution of **3** with CO (1 atm pressure, ambient temperature) rapidly results in the regeneration of **1** (see Scheme 1). The overall outcome of this reaction is

---

(12) Piermarini, G. J.; Mighell, A. D.; Weir, C. E.; Block, S. *Science* **1969**, *165*, 1250.

(13) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press, 1989, ISBN 0-08-022057-6.

(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(15) Iron, M. A.; Lucassen, A. C. B.; Cohen, H.; van der Boom, M. E.; Martin, J. M. L. *J. Am. Chem. Soc.* **2004**, *126*, 11699.

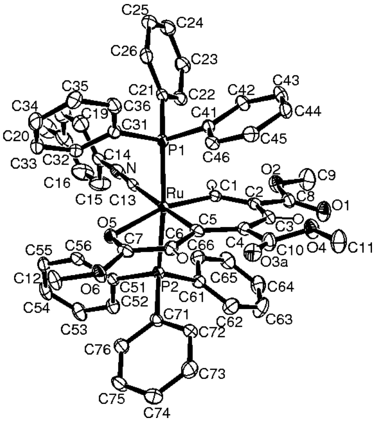


Figure 3. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Selected distances [Å]: Ru−C1 1.986(3), Ru−C5 2.092(4), Ru−C13 1.954(4), Ru−O5 2.266(2), C1−C2 1.368(5), C2−C3 1.437(5), C3−C4 1.376(5), C4−C5 1.475(5), C5−C6 1.376(5), C6−C7 1.437(5), O5−C7 1.242(4).

that the chloride ligand is substituted by CO and one of the protons on C6 is lost in a process that is formally the reverse of the reaction in which **3** is formed from **1**. We do not have any evidence that indicates whether substitution of chloride by CO occurs before or after the proton is lost from C6 during the reaction in which **1** is regenerated from **3**. In an analogous manner, treatment of **3** with *p*-tolylisocyanide gives the purple isocyanide-containing ruthenabenzofuran (or tethered ruthenacyclohexadiene) Ru[$C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)$](CNR)$(PPh_3)_2$ (**5**) (see Scheme 1). In the IR spectrum of **5** ν(CN) is observed at 2060 cm^{-1}. As might be expected, the ^{1}H and ^{13}C NMR spectra of **5** are similar to the corresponding spectra obtained for **1**. In the ^{1}H NMR spectrum of **5** H1 is observed at the low field position of 12.40 ppm (cf. 11.67 ppm in **1**), H6 is observed at 6.17 ppm (cf. 6.08 in **1**), and H3 is obscured by the PPh_3 resonances (7.26−7.46 ppm), as is the case for H3 in **1**. In the ^{13}C NMR spectrum of **5**, C1 and C5 are observed at the low field positions of 245.0 and 232.8 ppm, respectively (cf. 232.9 and 227.0, respectively, in **1**). The resonances of the other carbon atoms in the six-membered metallacyclic ring all appear in the aromatic region at 127.8 (C2), 147.4 (C3), and 121.1 (C4) ppm (cf. 128.5, 147.3, and 122.2 ppm, respectively, in **1**). The resonance for C6 (117.1 ppm) also falls in the aromatic region (cf. 119.1 ppm in **1**). It is noteworthy that the chemical shifts of H1 and C1/5 in **5** (and **1**) (ca. 12 and 235 ppm, respectively) are midway between the chemical shifts of the corresponding atoms in the ruthenabenzenes **2**, **3**, and [Ru[$CHC(PPh_3)CHC(PPh_3)CH$]$Cl_2(PPh_3)_2$]Cl[7] (ca. 16 and 280 ppm, respectively) and the chemical shifts of the corresponding atoms in simple, nonconjugated vinyl derivatives of ruthenium that bear bis(triphenylphosphine) and carbonyl or isocyanide ligands (ca. 8 and 175 ppm, respectively).[16]

The crystal structure of **5** was determined, and the molecular structure is shown in Figure 3. The same fused five- and six-membered bicyclic ring system with Ru at a bridgehead position that is present in **1** is also clearly evident in the structure of **5**. The atoms in the six-membered ruthenacyclic ring (Ru, C1−C5) are essentially coplanar, with the maximum displacement from the mean plane through these atoms being 0.064 Å. The atoms in the five-membered ring (Ru, C5−C7, O5) are also coplanar (maximum displacement from the mean plane through these five atoms is 0.037 Å). The bicyclic ring system is folded slightly about the Ru−C5 vector, and the angle between the two mean planes is 9.6°.

The Ru−C1 (1.986(3) Å) and Ru−C5 (2.092(4) Å) distances in **5** are both slightly longer than the corresponding distances in the cationic tethered ruthenabenzene **2** (1.933(4) and 2.045(5) Å, respectively), and the *trans*-influence of the CNR ligand is probably mostly responsible for the longer Ru−C(5). The C−C distances within the six-membered ruthenacyclic ring of **5** show considerably more alternation in length (C1−C2, 1.368(5); C2−C3, 1.437(5); C3−C4, 1.376(5); C4−C5, 1.475(5) Å) than do the corresponding distances in **2**. Nevertheless, the first three distances still all fall within the range observed for other metallabenzenes,[1] although the C4−C5 distance is closer to values normally associated with C−C single bonds. The C5−C6 (1.376(5) Å) and C6−C7 (1.437(5) Å) distances are also close to those commonly observed in aromatic systems. The bonding in the bicyclic ring system of **5** can be discussed in terms of the three valence bond structures **5A**−**5C** depicted in Chart 2. Three corresponding valence bond structures were used to discuss the bonding in the related osmabenzofuran Os[$C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)$](CS)$(PPh_3)_2$.[9] The alternation of the C−C distances in the ruthenabicyclic ring system of **5** points to a major contribution from valence bond structure **5C**. However, the C−C distances involving C1−4 and C5−7, which all fall within the normal aromatic range, indicate some contribution from **5A** and **5B**. This is supported by the ^{1}H and ^{13}C NMR chemical shifts of the ring atoms, which are consistent with a degree of delocalization within the ruthenabicyclic system. Accordingly, we favor a delocalized ruthenabenzofuran description for the bonding in **5** (and **1**[9]) rather than an alternative tethered ruthenacyclohexadiene description with localized double bonds.

Concluding Remarks

Tethered ruthenabenzenes are accessible through protonation of C6 in the five-membered ruthenacyclic ring of Ru[$C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)$](CO)$(PPh_3)_2$ (**1**). Thus, treatment of **1** with $HBF_4 \cdot OEt_2$ yields the blue cationic tethered ruthenabenzene [Ru[$C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)$](CO)$(PPh_3)_2$][$(BF_4)_2H$] (**2**), while treatment with HCl gives the green neutral tethered ruthenabenzene Ru[$C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)$]Cl$(PPh_3)_2$ (**3**). Both these ruthenabenzenes are stable in solution, and remarkably, **3** survives mostly unchanged on heating under reflux for several hours in a toluene/methanol solution that contains traces of HCl. Since calculations have shown that the coupling of the two metal-bound carbon atoms in simple metallabenzene models to give cyclopentadienyl ligands is a relatively low energy process for second-row transition metal derivatives,[15] the tethering arms and/or the methyl ester ring substituents in **2** and **3** probably provide important stabilizing effects.

Treatment of **3** with CN-*p*-tolyl causes HCl to be lost, and the isocyanide-containing compound Ru[$C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)$](CNR)$(PPh_3)_2$ (**5**) is formed. This is the isocyanide analogue of compound, **1**. On the basis of the structural and spectroscopic data for **5** (and **1**) some delocalization of the bonding within the fused ruthenabicyclic rings is apparent, and we therefore favor the description of these compounds as "ruthenabenzofurans".

Experimental Section

General Comments. Standard laboratory procedures were followed, as have been described previously.[16] The compound

---

[16] Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793.

$Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CO)(PPh_3)_2$ (**1**) was prepared according to the literature method.[10]

Infrared spectra (4000−400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin-Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were obtained operating at 400.1 (^1H), 100.6 (^{13}C), 376.5 (^{19}F), and 162.0 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm), ^{19}F NMR spectra to $CFCl_3$ (0.00 ppm), and ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

$[Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)](CO)(PPh_3)_2][(BF_4)_2H]$ (2). $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CO)(PPh_3)_2$ (**1**) (0.100 g) was dissolved in toluene (5 mL) at room temperature, giving a purple solution. $HBF_4 \cdot Et_2O$ (0.3 mL, 54% w/w solution) was then slowly added, causing the formation of a dark blue precipitate. This product was collected by filtration and recrystallized from dichloromethane/toluene to give pure **2** as dark blue crystals (0.042 g, 42%). Anal. Calc for $C_{49}H_{44}O_7P_2RuB_2F_8 \cdot (0.5CH_2Cl_2) \cdot (2.4H_2O)$: C, 50.93; H, 4.31. Found: C, 50.88; H, 4.21% (NMR spectroscopy showed the presence of ca. 0.5 molar equiv of CH_2Cl_2 of crystallization as well as ca. 2 molar equiv of water in the analytical sample. The crystal grown for X-ray structural analysis contained 0.3 molar equiv of CH_2Cl_2, 2.4 molar equiv of H_2O, and 0.5 molar equiv of toluene). IR (cm^{-1}): 1988 ν(CO); 1711, 1631 (CO_2CH_3). ^1H NMR ($CDCl_3$, δ): 2.73 (s, 2H, H*6*), 3.73 (s, 3H, H*10*), 3.83 (s, 3H, H*12*), 3.99 (s, 3H, H*13*), 7.15−7.54 (m, 30H, PPh_3), 8.83 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H3), 14.97 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H*1*). ^{13}C NMR ($CDCl_3$, δ): 52.0 (s, C*12*), 52.3 (s, C*10*), 53.2 (s, C*6*), 56.6 (s, C*13*), 129.1 (t′,[16] $^{2,4}J_{CP}$ = 10.3 Hz, *o*-PPh_3), 129.4 (t′, $^{1,3}J_{CP}$ = 48.9 Hz, *i*-PPh_3), 129.6 (s, C2), 130.8 (s, C*4*), 131.9 (s, *p*-PPh_3), 133.0 (t′, $^{3,5}J_{CP}$ = 11.3 Hz, *m*-PPh_3), 156.6 (s, C*3*), 163.9 (s, C*9*), 164.8 (s, C*11*), 185.9 (s, C*7*), 199.7 (t, $^2J_{CP}$ = 14.4 Hz, C*8*), 283.6 (t, $^2J_{CP}$ = 7.7 Hz, C*5*), 290.8 (t, $^2J_{CP}$ = 6.1 Hz, C*1*). ^{31}P NMR ($CDCl_3$, δ): 29.81. ^{19}F NMR ($CDCl_3$, δ): −154.49.

$Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)]Cl(PPh_3)_2$ (3). $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CO)(PPh_3)_2$ (**1**) (0.200 g) was heated under reflux in a solution of benzene (50 mL), methanol (12 mL), and trimethylsilyl chloride (0.180 mL) contained in a Pyrex flask illuminated with a 1000 W tungsten halogen lamp positioned 15 cm away from the flask. After 2 h more trimethylsilyl chloride (0.01 mL) was added to the flask, and the heating and illumination continued for a further 2.5 h. Over the course of the reaction the deep purple solution became bright green in color. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum of the solvent mixture dichloromethane/ethanol/trimethylsilyl chloride (100:2:0.05). This solution was then purified by column chromatography on silica gel using a solution of dichloromethane/ethanol/trimethylsilyl chloride (100:2:0.05) as eluant. The band that appeared dark brown on the column but eluted as a bright green solution was collected, and on removal to the solvent **3** was obtained as a green solid (0.157 g, 78%). MS (*m*/*z*, FAB$^+$, NBA): calcd for $C_{48}H_{43}{}^{35}ClO_6P_2{}^{102}Ru$, 914.12669 and $C_{48}H_{43}{}^{35}ClO_6P_2{}^{101}Ru$, 913.12792, found 914.12554, and 913.12946, respectively. Satisfactory elemental analysis could not be obtained, probably because of the small amounts of HCl that were required to be present in solution to stabilize this product and the poor crystallinity of solid samples. IR (cm^{-1}): 1720, 1586 (CO_2CH_3). ^1H NMR spectrum ($CDCl_3$, δ): 3.19 (s, 2H, H*6*), 3.59 (s, 3H, H*13*) 3.63 (s, 3H, H*12*), 3.67 (s, 3H, H*10*), 7.20−7.38 (m, 30H, PPh_3), 8.76 (d, $^4J_{HH}$ = 2.4 Hz, 1H, H*3*), 16.45 (dt, $^4J_{HH}$ = 2.7, $^3J_{HP}$ = 3.0 Hz, 1H, H*1*). ^{13}C NMR ($CDCl_3$, δ): 50.6 (s, C*12*), 51.3 (s, C*10*), 53.5 (s, C*13*), 56.2 (s, C*6*), 124.3 (s, C*4*), 126.2 (s, C2), 127.4 (t′, $^{2,4}J_{CP}$ = 9.5 Hz, *o*-PPh_3), 129.6 (s, *p*-PPh_3), 131.4 (t′, $^{1,3}J_{CP}$ = 43.4 Hz, *i*-PPh_3), 133.8 (t′, $^{3,5}J_{CP}$ = 10.7 Hz, *m*-PPh_3), 150.7 (s, C*3*), 165.2 (s, C*9*), 166.1 (s, C*11*), 182.6 (s, C*7*), 287.8 (t, $^2J_{CP}$ = 12.6 Hz, C*1*), 289.3 (t, $^2J_{CP}$ = 10.6 Hz, C*5*). ^{31}P NMR ($CDCl_3$, δ): 21.55.

$Ru[\eta^5\text{-}C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)]Cl(CO)(PPh_3)$ (4). Compound **4** can be obtained in low yield (ca. 10%) from a fast moving band eluted from the column described in the synthesis of **3** above. A higher yielding synthesis is as follows: $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CO)(PPh_3)_2$ (**1**) (0.200 g) and concentrated aqueous HCl (0.5 mL) were heated under reflux in a mixture of benzene (25 mL) and methanol (6 mL) for 5 h. After removal of the solvent under vacuum, the remaining crude solid (a mixture of unchanged **1**, **3**, and **4** in approximately equal amounts as determined by NMR spectroscopy) was dissolved in dichloromethane and a small amount of ethanol added. Upon removal of the dichloromethane under reduced pressure, **1** crystallized from solution and was removed by filtration. Excess hexane was added to the filtrate and the resulting solution left to stand for 16 h. During this time yellow crystals were deposited, and these were collected by filtration. Recrystallization from dichloromethane/hexane gave pure **4** as yellow crystals (0.030 g, 20%). Anal. Calc for $C_{31}H_{28}ClO_7PRu$: C, 54.75; H, 4.16. Found: C, 54.49; H, 4.37. MS (*m*/*z*, FAB$^+$, NBA): calcd for $C_{31}H_{28}{}^{35}ClO_7P^{102}Ru$, 680.03047 and $C_{31}H_{28}{}^{37}ClO_7P^{102}Ru$, 682.02752, found 680.03035 and 682.02890, respectively. IR (cm^{-1}): 1971 ν(CO); 1726, 1688, 1664 (CO_2CH_3). ^1H NMR ($CDCl_3$, δ): 2.88 (d, 1H, $^2J_{HH}$ = 17.8 Hz, H*6*), 3.31 (s, 3H, H*10*/H*12*/H*13*), 3.67 (s, 3H, H*10*/H*12*/H*13*), 3.78 (s, 3H, H*10*/H*12*/H*13*), 3.91 (d, 1H, $^2J_{HH}$ = 17.8 Hz, H*6*), 4.81 (d, 1H, $^4J_{HH}$ = 1.3 Hz, H*1*), 6.21 (d, 1H, $^4J_{HH}$ = 1.3 Hz, H*3*), 7.19 − 7.54 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 32.6 (s, C*6*), 51.8 (s, C*10*/C*12*/C*13*), 52.09 (s, C*10*/C*12*/C*13*), 52.1 (s, C*10*/C*12*/C*13*), 79.4 (s, C2/C*4*/C*5*), 82.3 (d, $^2J_{CP}$ = 9.1 Hz, C2/C*4*/C*5*), 88.1 (s, C*3*), 99.1 (s, C*1*), 112.4 (s, C2/C*4*/C*5*), 128.4 (d, $^2J_{CP}$ = 10.8 Hz, *o*-PPh_3), 130.6 (d, $^1J_{CP}$ = 51.1 Hz, *i*-PPh_3), 133.2 (s, *p*-PPh_3), 133.5 (d, $^3J_{CP}$ = 10.5 Hz, *m*-PPh_3), 164.6 (s, C*11*/C*9*/C*7*), 165.4 (s, C*11*/C*9*/C*7*), 170.4 (s, C*11*/C*9*/C*7*), 200.7 (d, $^2J_{CP}$ = 21.7 Hz, C*8*). ^{31}P NMR ($CDCl_3$, δ): 47.16.

$Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CHCO_2Me\text{-}5)](CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (5). A solution of *p*-tolyl isocyanide (0.013 g) in dichloromethane (3 mL) was added with stirring to a solution of $Ru[C_5H_2(CO_2Me\text{-}2)(CO_2Me\text{-}4)(CH_2CO_2Me\text{-}5)]Cl(PPh_3)_2$ (**3**) (0.100 g) in dichloromethane (5 mL) at room temperature. The color of the mixture turned instantly from green to dark purple-brown. After 5 min the solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel using dichloromethane/ethanol (100:2) as eluant. The major purple band was collected and a purple solid obtained by removal of the dichloromethane under reduced pressure. This was recrystallized from dichloromethane/ethanol to yield pure **5** as purple crystals (0.048 g, 48%). Anal. Calc for $C_{56}H_{49}NO_6P_2Ru \cdot (0.25CH_2Cl_2)$: C, 66.48; H, 4.91; N, 1.38. Found: C, 66.53; H, 4.88; N, 1.34. MS (*m*/*z*, FAB$^+$, NBA): calcd for $C_{56}H_{49}NO_6P_2{}^{102}Ru$, 995.20786 and $C_{56}H_{49}NO_6P_2{}^{104}Ru$, 997.20894, found 995.20793 and 997.20918, respectively. IR (cm^{-1}): 2060 ν(CNR); 1714, 1577 (CO_2CH_3). ^1H NMR ($CDCl_3$, δ): 2.27 (s, 3H, $CNC_6H_4CH_3$), 3.20 (s, 3H, H*13*), 3.53 (s, 3H, H*12*), 3.66 (s, 3H, H*10*), 5.95 (d, $^3J_{HH}$ = 8.3 Hz, 2H, H*14b*), 6.17 (t, $^4J_{HP}$ = 2.7 Hz, 1H, H*6*), 6.86 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H*14c*), 7.26 − 7.46 (m, 31H, PPh_3, and H3), 12.40 (dt, $^4J_{HH}$ = 1.8, $^3J_{HP}$ = 1.7 Hz, 1H, H*1*). ^{13}C NMR ($CDCl_3$, δ): 21.1 (s, C*15*), 50.3 (s, C*10*), 50.6 (s, C*12*), 51.3 (s, C*13*), 117.1 (s, C*6*), 121.1 (s, C*4*), 124.8 (s, C*14b*), 127.4 (t′, $^{2,4}J_{CP}$ = 9.1 Hz, *o*-PPh_3), 127.6 (s, C*14a*), 127.8 (s, C2), 129.1 (s, C*14c*), 129.3 (s, *p*-PPh_3), 133.1 (t′, $^{1,3}J_{CP}$ = 41.2 Hz, *i*-PPh_3), 134.2 (t′, $^{3,5}J_{CP}$ = 11.1 Hz, *m*-PPh_3), 136.3 (s, C*14d*), 147.4 (s, C*3*), 164.2 (s, C*11*), 168.6 (s, C9), 171.5 (t, $^2J_{CP}$ = 15.1 Hz C*8*), 178.8 (s, C*7*), 232.8 (t, $^2J_{CP}$ = 11.6 Hz, C*5*), 245.0 (t, $^2J_{CP}$ = 11.6 Hz, C*1*). ^{31}P NMR ($CDCl_3$, δ): 43.22.

Acknowledgment. We thank the Foundation for Research, Science and Technology for supporting this work through a postdoctoral fellowship to D.M.T.

Supporting Information Available: Crystal and refinement data in CIF format for compounds **2**, **4**, and **5** are available free of charge via the Internet at http://pubs.acs.org and from the Cambridge Crystallographic Data Centre (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) as supplementary publication nos. CCDC 699174−699176, respectively.

OM800857K