An Osmabenzofuran from Reaction between $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ and Methyl Propiolate and the C-Protonation of this Compound to Form a Tethered Osmabenzene

George R. Clark, Paul M. Johns, Warren R. Roper,* and L. James Wright*

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

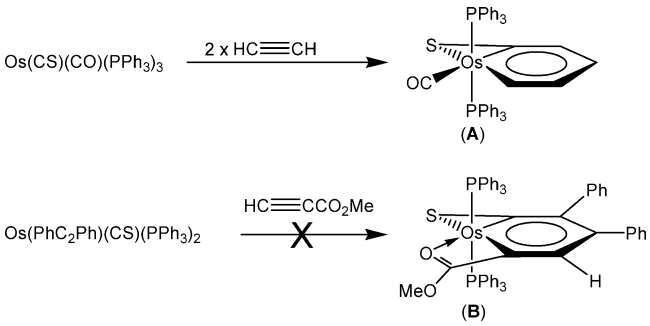
Received December 4, 2005

Reaction between the diphenylacetylene complex $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**) and two molecules of $HC{\equiv}CCO_2Me$ leads to a very stable, blue, osmabicylic complex with osmium at a bridgehead position. One way to consider this complex is as a metalla-aromatic molecule, viz., the osmabenzofuran $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**). The bicyclic ring system is remarkably robust, and heating this compound in ethanol at reflux with aqueous HCl effects only a transesterification of the ester function in the six-membered ring (at the 4-position), forming $Os[C_7H_2O(OMe\text{-}7)(CO_2Et\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**3**). Reaction of $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**) with pyridinium tribromide effects bromination in the five-membered ring of the osmabenzofuran at the 6-position to form $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**4**). Crystal structure determinations of **2**, **3**, and **4** confirm the osmabicyclic structure of each compound. Treatment of complex **2** with anhydrous trifluoroacetic acid results in protonation at carbon atom 6 to form the cationic, tethered osmabenzene $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]CF_3CO_2$ (**5**). This osmabenzene cation has also been isolated as the tri-iodide salt $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (**6**) and the crystal structure for this complex obtained. The spectroscopic and the structural data for **2**, **3**, and **4** give support for the osmabenzofuran formulation for these compounds. The spectroscopic data for **5** and **6** and the structural data for **6** support the tethered osmabenzene formulation for these two compounds.

Introduction

In the synthesis of the original osmabenzene, $Os(C_5H_4[S])(CO)(PPh_3)_2$ (compound **A** in Chart 1)[1], the OsC_5 ring was assembled from two ethyne molecules and a single carbon atom from the thiocarbonyl ligand already resident on the osmium in the starting material, $Os(CS)(CO)(PPh_3)_3$. At least two pathways can be envisaged for this reaction. The first, and more plausible, involves initial formation of an osmacyclobutenethione ring from combination of one ethyne molecule with CS, followed by ring expansion through reaction with a second ethyne to give an osmacyclohexadienethione, and finally aromatization of this intermediate through coordination of sulfur to osmium. There is precedent for the first step in this pathway in that reaction between $Os(CS)(CO)(PPh_3)_3$ and diphenylacetylene produces a complex with an osmacyclobutenethione ring,[2] and a recent computational study also provides support for this pathway.[3] Another pathway could involve initial formation of an osmacyclopentadiene from combination of two ethyne molecules on the osmium followed by ring expansion through insertion of the thiocarbonyl ligand into this five-membered ring. Either pathway depends for its success on the readiness with which the thiocarbonyl ligand undergoes insertion reactions. In previous work we have demonstrated that the thiocarbonyl ligand will insert easily into Os−H,[4] Os−C,[5] Os−Si,[6] and Os−B[7] bonds. With the exception of the Os−C example, insertion of a carbonyl ligand into these bonds has not been observed.

Chart 1



In view of the above discussion it seemed a reasonable expectation that the four-electron donor acetylene complex $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**)[2,8] might react with an activated acetylene such as methyl propiolate to give the di(phenyl)-substituted osmabenzene (**B**), as illustrated in Chart 1. A desirable attribute of methyl propiolate is that the oxygen of

* To whom correspondence should be addressed. E-mail: w.roper@auckland.ac.nz; lj.wright@auckland.ac.nz.

(1) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

(2) Elliott, G. P.; Roper, W. R. *J. Organomet. Chem.* **1983**, *250*, C5.

(3) 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.

(4) (a) Collins T. J.; Roper W. R. *J. Chem. Soc., Chem. Commun.* **1976**, 1044. (b) Roper W. R.; Town K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781.

(5) Clark G. R.; Collins T. J.; Marsden K.; Roper W. R. *J. Organomet. Chem.* **1978**, *157*, C23.

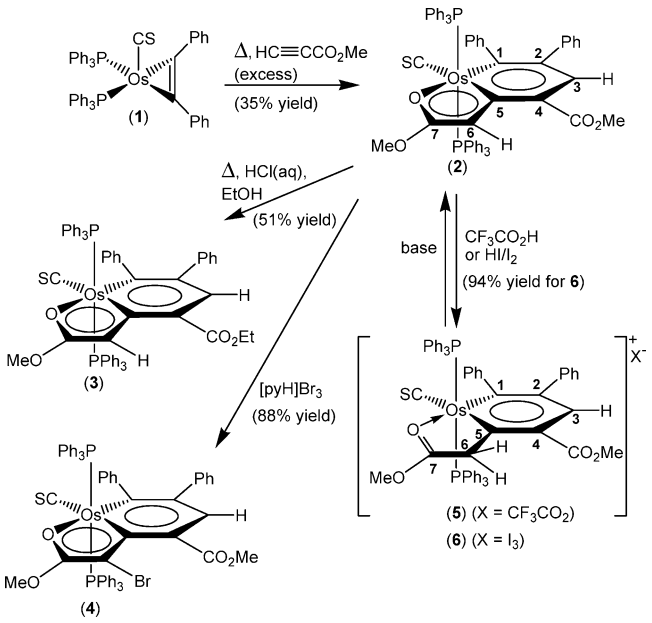
(6) Rickard C. E. F.; Roper W. R.; Salter D. M.; Wright L. J. *Organometallics* **1992**, *11*, 3931.

(7) Irvine G. J.; Lesley M. J. G.; Marder T. B.; Norman N. C.; Rice C. R.; Robins E. G.; Roper W. R.; Whittell G. R.; Wright L. J. *Chem. Rev.* **1998**, *98*, 2685.

(8) Burrell A. K.; Elliott G. P.; Rickard C. E. F.; Roper W. R. *Appl. Organomet. Chem.* **1990**, *4*, 535.

10.1021/om0510371 CCC: $33.50
Publication on Web 02/18/2006

Scheme 1



the carbonyl group in the ester function could coordinate to the osmium center, thus resulting in a coordinatively saturated osmabenzene. In fact the reaction does not follow this pathway. However, a six-membered OsC_5 ring is formed with two carbon atoms from diphenylacetylene, two carbon atoms from methyl propiolate, and the fifth carbon atom, surprisingly not through incorporation of the CS ligand, but rather through inclusion of one carbon atom (formally as a vinylidene fragment) from a second methyl propiolate molecule.

Herein, we report (i) the reaction between $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**) and two molecules of $HC{\equiv}CCO_2Me$, which leads to the osmabenzofuran $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**), (ii) the reaction of **2** with EtOH in the presence of aqueous HCl, which leaves the metal-bound ester function unchanged but effects transesterification of the other ester function on the six-membered ring into the corresponding ethyl ester, leading to $Os[C_7H_2O(OMe\text{-}7)(CO_2Et\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**3**), (iii) the bromination of **2** through an electrophilic substitution of the osmabenzofuran to give $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**4**), (iv) the protonation of **2** with trifluoroacetic acid at the 6-position to convert **2** to the tethered osmabenzene $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]CF_3CO_2$ (**5**), (v) the protonation of **2** with HI/I_2 at the 6-position to convert **2** to the tethered osmabenzene $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (**6**), (vi) the crystal structure determinations of **2**, **3**, and **4**, which confirm the osmabenzofuran structures and provide evidence for delocalization within both rings of all three compounds, and (vii) the crystal structure of **6**, which confirms the osmabenzene structure and gives evidence for delocalization within the osmabenzene ring.

Results and Discussion

1. Reaction between $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (1) and $HC{\equiv}CCO_2Me$ to Form $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (2) and the Crystal Structure of this Compound. As depicted in Scheme 1, reaction between $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**) and an excess of methyl propiolate proceeds slowly in benzene under reflux to give a blue-colored, stable product that incorporates two molecules of methyl propiolate, $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**), in 35% yield after chromatography. The written formula for this product is based on a consideration of the core metallabicycle (with osmium at a bridgehead) as an osmabenzofuran, $Os[C_7H_6O]L_3$. The ring-numbering scheme used to identify the position of the substituents (see Scheme 1) was chosen to retain positions C(1)−C(5) as a constant to facilitate discussion and comparison of spectroscopic and structural data between all the compounds reported in this paper, osmabenzofurans (complexes **2**, **3**, and **4**) and osmabenzenes (complexes **5** and **6**), alike.

The case for considering complexes **2**−**4** as osmabenzofurans is developed below after presentation of the spectroscopic and structural data for these compounds. Full spectroscopic data for **2** and the other compounds reported in this paper are in the Experimental Section 4. The IR spectrum of **2** shows a strong band at 1229 cm^{-1} (ν(CS)) indicating that the complex retains a terminal CS ligand. It is quite remarkable, in view of the propensity of the CS ligand to participate in migratory insertion reactions, that the CS ligand in this reaction does not become involved with either the diphenylacetylene or the methyl propiolate in the ring-forming processes leading to **2**. Other IR bands at 1695 and 1569 cm^{-1} are consistent with the presence of an ester function in the complex. The ^1H NMR spectrum of **2** reveals signals for two different methyl groups at 3.25 and 3.51 ppm. There are also signals at 6.51 and 6.99 ppm assigned to ring protons at positions 6 and 3, respectively. Remarkably, the proton at C(6) is a triplet ($^4J_{CP} = 3.6$ Hz), which collapses to a singlet in the ^{31}P-decoupled spectrum. The ^{13}C NMR spectrum of **2** reveals three very low-field triplet signals, one appropriate for the CS ligand at 291.1 ppm ($^2J_{CP} = 11.2$ Hz) and two others for C(1) at 196.4 ($^2J_{CP} = 8.6$ Hz) and C(5) at 218.9 ppm ($^2J_{CP} = 11.2$ Hz). The chemical shifts of the latter signals are appropriate for osmium-bound carbon atoms, where there is a significant degree of multiple Os−C bonding. In fact these shifts are close to those for the classic osmabenzene $Os[C_5H_4(SMe\text{-}1)]I(CO)(PPh_3)_2$,[9] which for C(1) and C(5) are at 237.5 ($^2J_{CP} = 9.1$ Hz) and 221.6 ppm ($^2J_{CP} = 6.3$ Hz), respectively. There is also a triplet signal in the aromatic region, at 123.6 ppm ($^3J_{CP} = 4.2$ Hz) for C(6). The long-range phosphorus coupling to C(6) and the proton attached to C(6) also suggest extensive electron delocalization through the ring system. All of the above spectroscopic data are consistent with the delocalized structure for **2** depicted in Scheme 1, and this was further substantiated by a crystal structure determination.

The molecular structure of **2** is shown in Figure 1. The crystal data and refinement details for **2** and for the other crystal structures reported in this paper are available in the Supporting Information, and selected bond lengths and angles for **2** and for the other structures discussed below are all listed in Table 1. The overall geometry is approximately octahedral with the two triphenylphosphine ligands arranged mutually *trans*. The structure shows the thiocarbonyl ligand bound at the short Os−C distance of 1.846(3) Å. The $Os[C_7O]$ bicyclic ring system (an osmabenzene with a fused furan ring with Os at a bridgehead position) is essentially planar (the mean deviation from the least squares plane through the nine ring atoms is 0.1028 Å). The Os−C(1) and Os−C(5) distances are 2.068(3) and 2.142(3) Å, respectively. The longer Os−C(5) distance can be attributed to the pronounced *trans* influence of the CS ligand; nevertheless the distances are comparable with other Os−C distances found in osmabenzene systems.[1,9] In Chart 2 are drawn the contributing valence bond structures for complex **2**. The observed C−C distances around the six-membered ring suggest the importance

(9) Rickard C. E. F.; Roper W. R.; Woodgate S. D.; Wright L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 750.

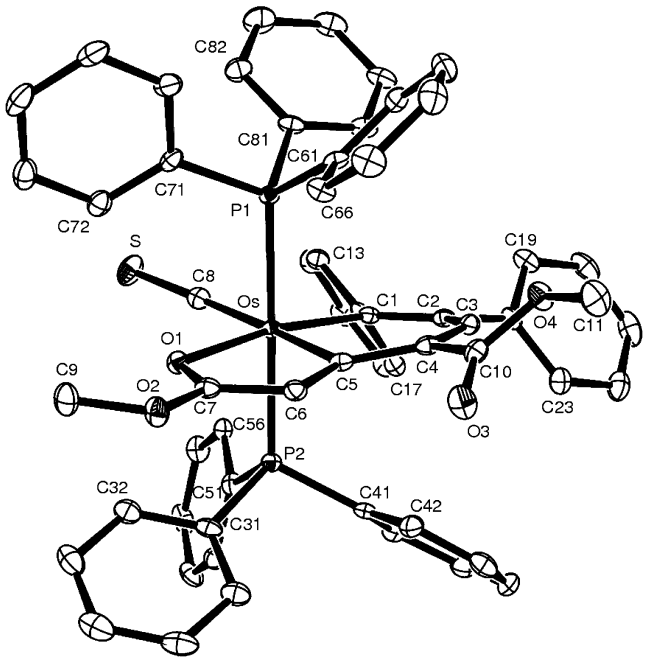


Figure 1. Molecular geometry and atomic numbering scheme for $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**).

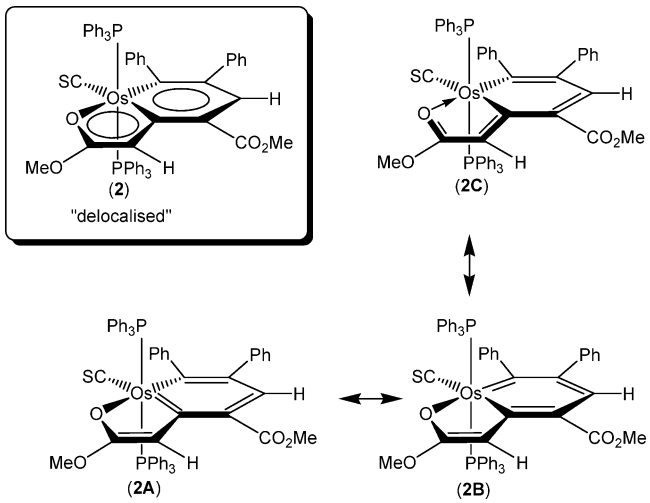
of a contribution from **2C**, although in fact these C−C distances are quite close to those commonly observed in aromatic systems. On the other hand the similarity of the observed C(5)−C(6) and C(6)−C(7) distances at 1.371(3) and 1.416(4) Å, respectively, points to considerable delocalization within the "osmafuran" part of the ring system, and this is not consistent with localized double and single bonds as is required by **2C** alone. This suggests that valence bond structures **2A** and **2B** must also contribute to some extent. Accordingly, we favor a delocalized description of the bonding as depicted in **2** (Chart 2), i.e, an osmabenzofuran. Iridafurans have been ascribed delocalized structures on the basis of both spectroscopic properties and structural data as well as chemical behavior appropriate for aromatic systems, viz., electrophilic aromatic bromination.[10]

A ruthenium complex with the same basic metallabicyclic skeleton as discussed above for the osmabenzofuran **2** was formed from the reaction between $RuH_2(CO)(PPh_3)_3$ and methyl propiolate.[11] Using the same system as above for writing the formula of this compound as a ruthenabenzofuran, this compound could be written as $Ru[C_7H_3O(CO_2Me\text{-}2)(CO_2Me\text{-}4)(OMe\text{-}7)](CO)(PPh_3)_2$. However, the authors of this paper chose to depict the structure of this compound using localized bonds as in **C** (M = Ru) in Chart 3, i.e., as a tethered ruthenacyclohexadiene. Re-examination of the spectroscopic properties of this compound indicate that, like the osmabenzofuran reported here, it is reasonably represented as a ruthenabenzofuran. Key features are the ^{1}H NMR chemical shift for the proton on C(1) at 11.67 ppm, a value now recognized as being typical for metallabenzene systems,[12] and the ^{13}C NMR chemical shifts for the ruthenium-bound ring carbon atoms at the very low-field values of 232.9 (t, $^2J_{CP}$ = 11.6 Hz, Ru*C*H) and 227.0 (t, $^2J_{CP}$ = 12.6 Hz, Ru*C*),[13] values that are again appropriate for metallabenzene systems. The structural data originally reported can be accommodated equally well using the ruthenabenzofuran formulation. A second crystal structure of this same compound, which is more accurate, has been reported, and the authors comment upon the delocalization apparent in the five-membered ring.[14] An iron analogue of this ruthenium compound is also

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 2, 3, 4, and 6

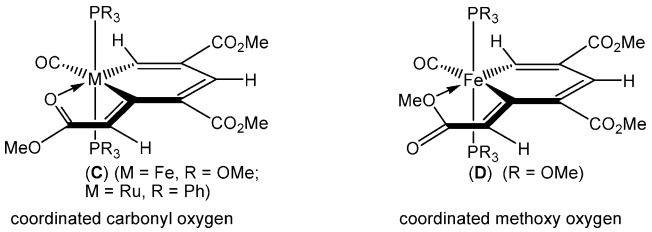
	2	**3**	**4**	**6**
		Bond Lengths		
Os−C(8)	1.846(3)	1.866(4)	1.853(4)	1.901(6)
Os−C(1)	2.068(3)	2.068(4)	2.055(4)	1.996(5)
Os−C(5)	2.142(3)	2.162(4)	2.135(4)	2.103(6)
Os−O(1)	2.2178(17)	2.232(3)	2.234(3)	2.221(4)
Os−P(1)	2.3834(7)	2.4060(10)	2.3844(10)	2.4349(15)
Os−P(2)	2.3902(7)	2.4279(10)	2.4167(11)	2.4341(15)
Br−C(6)			1.919(4)	
S−C(8)	1.588(3)	1.599(4)	1.571(4)	1.566(6)
O(1)−C(7)	1.250(3)	1.264(5)	1.244(5)	1.226(8)
O(2)−C(7)	1.333(3)	1.350(5)	1.313(5)	1.322(7)
C(1)−C(2)	1.376(4)	1.406(6)	1.389(6)	1.450(8)
C(2)−C(3)	1.442(3)	1.450(5)	1.433(6)	1.374(8)
C(3)−C(4)	1.359(4)	1.380(6)	1.368(6)	1.438(8)
C(4)−C(5)	1.436(4)	1.466(6)	1.438(6)	1.375(8)
C(5)−C(6)	1.371(3)	1.375(6)	1.363(6)	1.507(8)
C(6)−C(7)	1.416(4)	1.424(6)	1.438(6)	1.495(9)
		Bond Angles		
C(8)−Os−C(1)	99.25(11)	100.42(16)	95.84(17)	97.3(2)
C(8)−Os−C(5)	167.68(10)	166.41(16)	171.86(17)	170.2(2)
C(1)−Os−C(5)	92.30(10)	93.16(15)	91.80(16)	91.9(2)
C(8)−Os−O(1)	92.76(9)	89.99(14)	95.65(15)	93.3(2)
C(1)−Os−O(1)	167.37(8)	169.40(12)	168.39(13)	169.31(19)
C(5)−Os−O(1)	76.06(8)	76.42(13)	76.82(13)	77.56(19)
C(8)−Os−P(1)	86.91(8)	91.36(12)	90.53(12)	88.88(17)
C(1)−Os−P(1)	95.39(7)	90.17(10)	90.25(10)	92.72(16)
C(5)−Os−P(1)	87.73(7)	88.13(11)	86.63(11)	93.96(16)
O(1)−Os−P(1)	89.11(5)	87.58(7)	91.36(8)	86.14(11)
C(8)−Os−P(2)	95.33(8)	92.29(12)	89.53(12)	85.14(18)
C(1)−Os−P(2)	87.58(7)	93.95(11)	99.41(11)	95.46(16)
C(5)−Os−P(2)	89.41(7)	87.18(10)	91.98(11)	90.75(16)
O(1)−Os−P(2)	87.43(5)	87.57(7)	78.96(8)	86.73(11)
P(1)−Os−P(2)	175.96(2)	173.92(4)	170.28(4)	170.42(5)
C(7)−O(1)−Os	111.75(16)	111.1(3)	111.4(3)	114.2(4)
C(2)−C(1)−Os	123.10(18)	123.4(3)	124.8(3)	123.8(4)
C(1)−C(2)−C(3)	125.8(2)	125.3(4)	124.7(4)	125.3(5)
C(4)−C(3)−C(2)	130.9(2)	131.8(4)	131.7(4)	128.9(5)
C(3)−C(4)−C(5)	122.5(2)	122.1(4)	121.5(4)	122.0(5)
C(6)−C(5)−C(4)	123.0(2)	123.7(4)	123.6(4)	120.7(5)
C(6)−C(5)−Os	113.91(19)	113.5(3)	111.7(3)	114.0(4)
C(4)−C(5)−Os	122.41(17)	122.6(3)	124.5(3)	124.7(4)
C(5)−C(6)−C(7)	115.1(2)	115.4(4)	117.4(4)	110.1(5)
C(5)−C(6)−Br			126.9(4)	
C(7)−C(6)−Br			115.7(3)	
O(1)−C(7)−C(6)	123.0(2)	123.5(4)	121.1(4)	122.8(5)
S−C(8)−Os	170.78(17)	169.0(3)	174.4(3)	172.8(4)

Chart 2

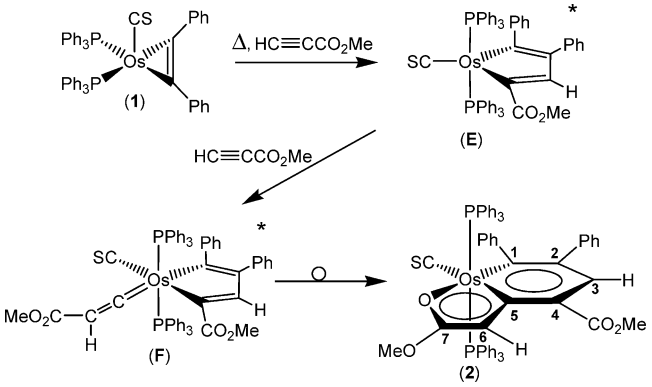


(10) Bleeke J. R.; New P. R.; Blanchard J. M. B.; Haile T.; Beatty A. M. *Organometallics* **1995**, *14*, 5127.
(11) Yamazaki H.; Aoki K. *J. Organomet. Chem.* **1976**, *122*, C54.
(12) Bleeke J. R. *Chem. Rev.* **2001**, *101*, 1205.
(13) Roper W. R.; Tonei D. M.; Wright L. J. Unpublished work.

Chart 3



Scheme 2



known and, interestingly, exists as two geometrical isomers, one identical to **C** (M = Fe, R = OMe) in Chart 3 with the five-membered ring closed by the carbonyl oxygen[15] and the other with the five-membered ring closed by the methoxy oxygen (**D** in Chart 3).[16]

While we do not have any conclusive evidence for the mechanism of formation of **2**, it can be speculated that a sequence such as that depicted in Scheme 2 is plausible. Since the thiocarbonyl ligand is still bound as a terminal ligand in the final product **2**, it is very likely that any intermediates also retain the unchanged thiocarbonyl ligand. Accordingly, a reasonable first intermediate is **E** in Scheme 2, which is a coordinatively unsaturated osmacyclopentadiene. This could incorporate further methyl propiolate as a vinylidene ligand as shown in intermediate **F**. Finally, insertion of the vinylidene ligand into the five-membered ring, probably in a concerted process that involves bond formation between the ester carbonyl O atom and the osmium, gives the observed product **2**. There is precedent for the vinylidene insertion step in the work of Chin and Lee, where they propose vinylidene insertion as a step in the conversion of iridacyclopentadienes to iridabenzenes.[17]

2. Reaction between Os[C_7H_2O(OMe-7)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$ (2) and EtOH/HCl to Give Os[C_7H_2O(OMe-7)(CO_2Et-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$ (3) and the Crystal Structure of this Compound. If **2C** in Chart 2 is an important valence bond structure for complex **2**, then it might have been expected that reaction with acids could occur with protonation at C(6) and with formation of an osmabenzene system. In a related iridacyclohexadiene system with a C(5)−C(6) double bond it has been shown that protonation occurs at C(6) to give an iridabenzene.[17] Accordingly, in an NMR experiment, complex **2** was treated with concentrated aqueous HCl. At room temperature, observation of the ^{1}H NMR spectrum revealed that protonation does occur at C(6). This is indicated by disappearance of the triplet at 6.51 ppm (H(6)) and the appearance of a methylene signal at 2.97 ppm. Addition of D_2O to this sample brings about disappearance of the methylene signal, and the signal at 6.51 does not reappear, indicating rapid reversible protonation resulting in deuterium exchange at C(6). Experiments described below with nonaqueous acids allow structural characterization of the protonated material and confirm that C(6) is the site of protonation. In experiments using aqueous HCl, attempts to isolate the protonated material by addition of ethanol resulted only in deprotonation and recovery of unchanged complex **2**. However, when **2** was heated with excess concentrated aqueous HCl in a benzene/ethanol mixture at reflux for 1 h, there was an observable reaction and a blue-green crystalline solid (**3**) could be isolated. This material retained a terminal CS ligand, as was apparent from a ν(CS) band at 1228 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum of **3** was almost identical to that of **2** except that instead of two methyl signals there appeared signals for one methyl and one ethyl group. The ^{13}C NMR spectrum also revealed the presence of one methyl and one ethyl group but in all other respects was closely similar to that of **2**. Either the methoxy group on the ester function at C(4) has been exchanged for an ethoxy group, or the methoxy function on C(7) has been exchanged for an ethoxy. The methyl signal in **2** that disappears was at 3.51 ppm and had been assigned to the ester function on C(4). It therefore seemed very likely that the conversion of **2** to **3** involved only the transesterification of the ester function at C(4). This was subsequently confirmed by the X-ray crystal structure to be described below. The fact that the fused furan ring system in complex **2** withstood the vigorous thermal and acidic conditions used in the formation of **3** is a testimony to the remarkable stability of this extended metal−aromatic system and is further justification for regarding both **2** and **3** as osmabenzofurans.

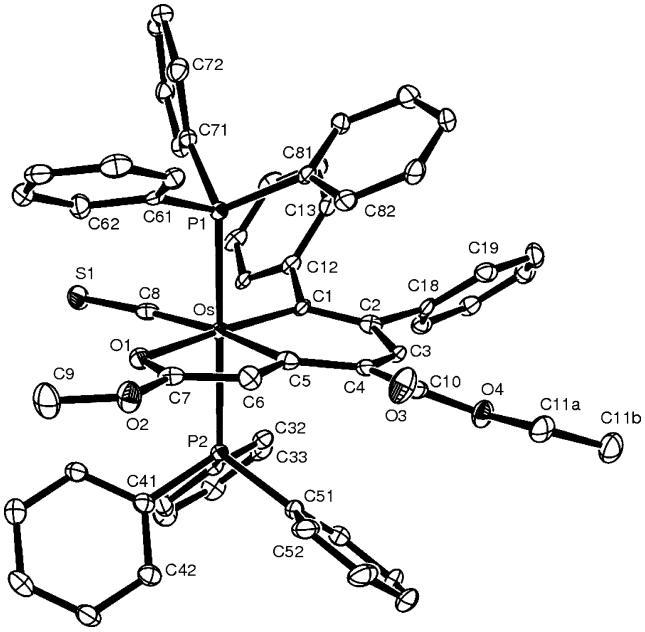


Figure 2. Molecular geometry and atomic numbering scheme for Os[C_7H_2O(OMe-7)(CO_2Et-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$ (**3**).

The molecular structure of **3** is shown in Figure 2, and selected bond lengths and angles for **3** are listed in Table 1. The overall geometry is almost the same as that for complex **2** apart from the orientation of the ring substituents. The structure confirms that the ethoxy group is part of the ester function attached to C(4). The structure shows the thiocarbonyl ligand bound at the short Os−C distance of 1.866(4) Å. The Os[C_7O]

(14) 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.
(15) Grössmann U.; Hund H.-U.; Bosch H. W.; Schmalle H.; Berke H. *J. Organomet. Chem.* **1991**, *408*, 203.
(16) Birk R.; Grössmann U.; Hund H.-U.; Berke H. *J. Organomet. Chem.* **1988**, *345*, 321.
(17) Chin C. S.; Lee H. *Chem. Eur. J.* **2004**, *10*, 4518.

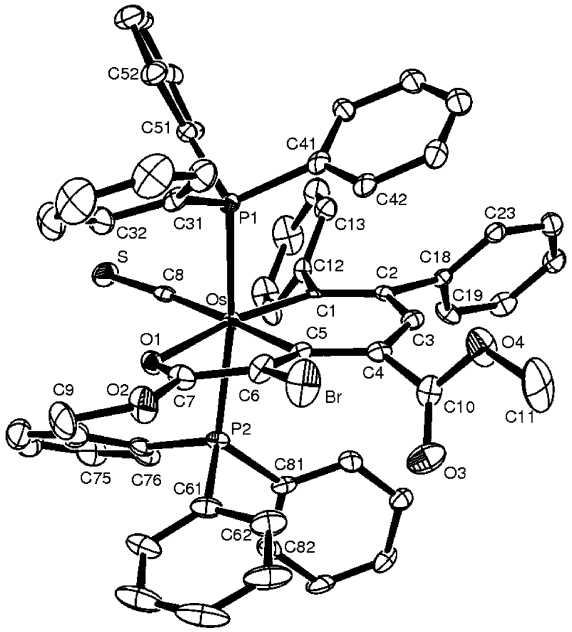


Figure 3. Molecular geometry and atomic numbering scheme for $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**4**).

bicyclic ring system is again essentially planar (the mean deviation from the least squares plane through the nine ring atoms is 0.0759 Å). The Os−C(1) and Os−C(5) distances and the C−C distances around the six-membered ring are all closely similar to those for complex **2**. A good description of the bonding is again as an osmabenzofuran.

3. Reaction of $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (2) with Pyridinium Tribromide to Form $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (4) and the Crystal Structure of this Compound. The robustness of the metalla-bicyclic ring system in complex **2**, revealed above in Section 2, prompted us to consider the possibility of the ring system undergoing an electrophilic substitution reaction. Clearly, the six-membered ring has only one site available for substitution, and this does not look particularly favorable because of the steric protection afforded by the two adjacent substituents. However, the C(6) site in the five-membered furan ring is a good possibility, and indeed this is the very position that has been brominated in a study of iridafurans.[10] Accordingly, complex **2** was treated with pyridinium tribromide, and this gave an 88% yield of metallic green crystals of the brominated compound $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**4**) (see Scheme 1). The terminal CS ligand in **4** showed a ν(CS) band at 1244 cm^{-1} in the IR spectrum, a value slightly higher than in **2**, indicating that the electron-withdrawing effect of the bromide substituent is transmitted through the ring system to the osmium atom. In the ^1H NMR spectrum the signal for the proton on C(6) in complex **2** is no longer present, suggesting that this is the site of bromination, and this was confirmed by a crystal structure determination of **4**. The resonance for the proton on C(3) is at 6.31 ppm, shifted from the position of 6.99 ppm in **2**. Other features of the ^1H NMR spectrum are closely similar to those observed for **2**.

The molecular structure of **4** is shown in Figure 3, and selected bond lengths and angles for **4** are listed in Table 1. The overall geometry is almost the same as that for complexes **2** and **3** apart from the orientation of the ring substituents. The structure confirms that bromination has occurred at C(6) and the C(6)−Br distance is 1.919(4) Å. The structure shows the thiocarbonyl ligand bound at the short Os−C distance of 1.853(4) Å. The $Os[C_7O]$ bicyclic ring system is again essentially planar (the mean deviation from the least squares plane through the nine ring atoms is 0.0758 Å). The Os−C(1) and Os−C(5) distances and the C−C distances around the six-membered ring are all closely similar to those for complexes **2** and **3**. The sum of the three angles at C(6) [C(5)−C(6)−C(7), 117.4(4)°; C(5)−C(6)−Br, 126.9(4)°; C(7)−C(6)−Br, 115.7(3)°] is exactly 360°. A good description of the bonding is again as an osmabenzofuran.

4. Reaction of 2 with Either Trifluoroacetic Acid or HI/I_2 to Form Either $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]CF_3CO_2$ (5) or $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (6) and the Crystal Structure of 6. The reversible protonation of **2** and the bromination of **2** described above indicate that C(6) is a preferred site for electrophilic attack. Addition of any electrophile to C(6) would result in a product in which the delocalization around the five-membered ring is disrupted, leaving the system as a tethered, but nevertheless unambiguous, osmabenzene. Since aqueous HCl had not been effective in this respect (see above), anhydrous acids were investigated. Upon addition of trifluoroacetic acid to **2**, there was an immediate color change to a green solution, but all attempts to isolate the green compound, using hydroxylic solvents, resulted only in the reformation of complex **2**. Therefore, anhydrous trifluoroacetic acid was added to a $CDCl_3$ solution of **2** in an NMR tube and the spectroscopic data for the green compound was recorded. The ^1H NMR spectrum shows that the triplet resonance for the C(6) proton at 6.51 ppm in complex **2** disappears and a new singlet signal integrating for two protons appears at 2.97 ppm. The loss of phosphorus coupling is entirely consistent with the loss of delocalization in the five-membered ring, which protonation at C(6) would require. Another significant change in the ^1H NMR spectrum is that the resonance for the proton on C(3) now appears at the low-field position of 8.36 ppm; this shift can be explained both by the greater aromaticity expected in the resulting osmabenzene ring and by the presence of the overall positive charge in $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]^+$. The downfield shift of the C(3) proton could also be influenced by the particular orientation of the adjacent substituents at C(2) and C(4). The ^{13}C NMR spectrum complements these observations in that C(6) now appears at 52.6 ppm (for complex **2** C(6) appears at 123.6 ppm) and the signal inverts in the DEPT 135 spectrum, indicating a methylene group. The resonance for C(3) is at 153.6 ppm. The corresponding values for C(2) and C(4) are 148.6 and 135.4 ppm, respectively. These values are appropriate for metallabenzene systems.[12] The most pronounced shifts are for C(1) and C(5), which now appear as triplets at 280.3 ($^2J_{CP}$ = 4.1 Hz) and 243.9 ($^2J_{CP}$ = 8.1 Hz). The corresponding values for complex **2** are 196.4 ppm ($^2J_{CP}$ = 8.6 Hz) and 218.9 ppm ($^2J_{CP}$ = 11.2 Hz), respectively. There is also a triplet signal at 294.8 ppm ($^2J_{CP}$ = 11.6 Hz) for the CS ligand.

Treatment of **2** with gaseous HI, contaminated with small amounts of iodine from oxidation of the HI, also resulted in a color change to green, and with this acid it was possible to isolate dark green crystals of the tri-iodide salt of protonated **2**, $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (**6**). The ^1H, ^{13}C, and ^{31}P NMR spectral data for compound **6** are almost identical to those discussed above for the trifluoroacetate salt. A crystal structure determination was carried out to confirm the conclusions derived from the spectroscopic data.

The molecular structure of the cation from **6** is shown in Figure 4, and selected bond lengths and angles for **6** are listed in Table 1. The overall geometry is related to that observed for the other complexes discussed in this paper. The structure

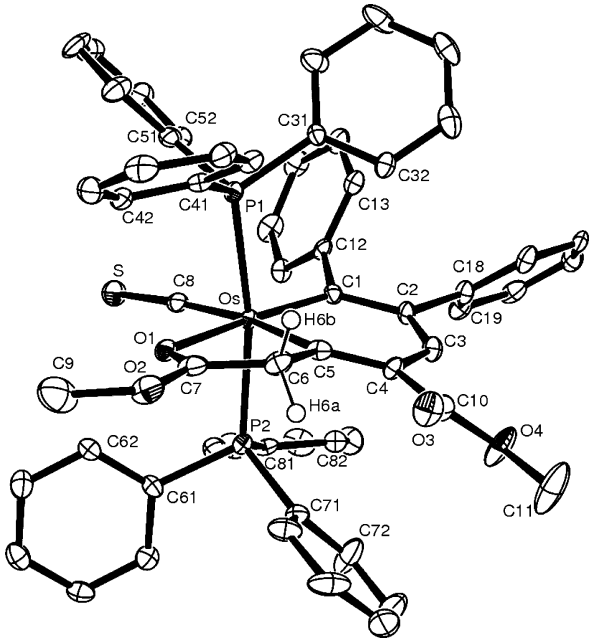


Figure 4. Molecular geometry and atomic numbering scheme for $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (**6**).

confirms that protonation has occurred at C(6), and the C(5)−C(6) and C(6)−C(7) distances are now 1.507(8) and 1.495(9) Å, respectively, showing that these are now single bonds. The Os−O distance at 2.221(4) Å is little changed from the corresponding values seen in **2** (2.2178(17) Å), **3** (2.232(3) Å), and **4** (2.234(3) Å); however, the C(7)−O(1) distance of the coordinated carbonyl group is shorter in **6** (1.226(8) Å) than in the other three structures. The structure shows that the thiocarbonyl ligand is bound at the slightly longer (compared to **2**, **3**, and **4**) Os−C distance of 1.901(6) Å, as would be expected for a cation. The Os[C_7O] bicyclic ring system is now significantly distorted from planarity (the mean deviation from the least squares plane through the nine ring atoms is 0.1397 Å), the atom showing the greatest displacement being C(6), which is 0.25 Å from the mean plane. On the other hand the Os[C_5] metallabenzene ring is relatively planar, with the mean deviation from the least squares plane through the six ring atoms being 0.0915 Å. The Os−C(1) (1.996(5) Å) and Os−C(5) (2.103(6) Å) distances and the C−C distances around the six-membered ring are all appropriate for metallabenzene systems.[12] A good description of the bonding from the structural and spectroscopic data is as a tethered osmabenzene.

Concluding Remarks

It has been demonstrated that beginning with the coordinated diphenylacetylene complex $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**) a metal-mediated cyclization reaction with two molecules of $HC{\equiv}CCO_2Me$ assembles an osmabicylic complex with osmium at a bridgehead position. This blue complex, which demonstrates great stability, is formulated on the basis of spectroscopic and structural data as a fused ring metalla-aromatic molecule, the osmabenzofuran $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**2**). Complex **2** can be transesterified with ethanol/HCl at the ester function at the 4-position of the six-membered ring, forming $Os[C_7H_2O(OMe\text{-}7)(CO_2Et\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**3**), and is readily brominated at C(6) in the osmafuran ring to give $Os[C_7HO(OMe\text{-}7)(Br\text{-}6)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (**4**). Complex **2** is also protonated at C(6) by the anhydrous acids trifluoroacetic acid and HI/I_2, so disrupting the delocalization in the five-membered ring and forming the cationic, tethered osmabenzene complexes $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]CF_3CO_2$ (**5**) and $[Os[C_5H(CH_2CO_2Me\text{-}5)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2]I_3$ (**6**), respectively. This protonation is reversible, and spectroscopic and structural data indicate the validity of regarding the protonated species as osmabenzenes.

Experimental Section

General Comments. Standard laboratory procedures were followed as have been described previously.[18] The compound $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$[2,8] was prepared by the literature method.

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 either a Bruker DRX 400 or a Bruker AVANCE 300 at 25 °C. For the Bruker DRX 400, ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 400.1 (^{1}H), 100.6 (^{13}C), and 162.0 (^{31}P) MHz, respectively. For the Bruker AVANCE 300, ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 300.13 (^{1}H), 75.48 (^{13}C), and 121.50 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^{1}H 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 $CDCl_3$ (77.00 ppm), and ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

Preparation of $Os[C_7H_2O(OMe\text{-}7)(CO_2Me\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (2). In a Schlenk tube, under nitrogen, $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ (**1**) (0.131 g, 0.119 mmol), $HC{\equiv}CCO_2Me$, and methyl propiolate (373 μL, 0.350 g, 4.16 mmol) in benzene (14 mL) were heated under reflux for 60 min. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum of dichloromethane and then purified by chromatography on a silica gel column using dichloromethane as eluant. A yellow band containing unreacted **1** (14 mg) was eluted first. This was followed by a blue band, which was collected, and the blue solid obtained by removal of the solvent was recrystallized from dichloromethane/ethanol to yield pure **2** (57 mg, 35%), *m*/*z* 1104.22974 and 1106.23577; $C_{59}H_{48}O_4{}^{190}OsP_2S$ and $C_{59}H_{48}O_4{}^{192}OsP_2S$ require 1104.23331 and 1106.23635, respectively. Anal. Calc for $C_{59}H_{48}O_4OsP_2S$: C, 64.12; H, 4.38. Found: C, 64.17; H, 4.58. IR (cm^{-1}): 1695, 1569 (methyl ester); 1229s ν(CS). ^{1}H NMR ($CDCl_3$, δ): 3.25 (s, 3H, OCH_3 on C7), 3.51 (s, 3H, CO_2CH_3 on C4), 5.87−6.89 (m, 10H, *Ph* on C1 and C2), 6.51 (t which collapses to singlet on ^{31}P decoupling, 1H, *H*6, $^4J_{CP}$ = 3.6 Hz), 6.99 (s, 1H, *H*3), 7.19−7.34 and 7.47−7.54 (m, 30H, P*Ph*$_3$). ^{13}C NMR ($CDCl_3$, δ): 50.2 (s, CO_2CH_3 on C4), 52.7 (s, OCH_3 on C7), 123.5, 124.3, 125.0, 126.6, 129.3, 130.8, 148.6, 159.7 (all s, *Ph* on C1 and C2), 123.6 (t, *C*6, $^3J_{CP}$ = 4.2 Hz), 124.4 (s, *C*4), 127.1 (t′,[18] $^{2,4}J_{CP}$ = 9.7 Hz, *o*-P*Ph*$_3$), 129.5 (s, *p*-P*Ph*$_3$), 131.6 (t′, $^{1,3}J_{CP}$ = 49.0 Hz, *i*-P*Ph*$_3$), 135.4 (t′, $^{3,5}J_{CP}$ = 9.7 Hz, *m*-P*Ph*$_3$), 137.6 (s, *C*2), 158.1 (s, *C*3), 168.1 (s, *C*O_2Me on C4), 184.7 (s, *C*7), 196.4 (t, $^2J_{CP}$ = 8.6 Hz, *C*1), 218.9 (t, $^2J_{CP}$ = 11.2 Hz, *C*5), 291.1 (t, $^2J_{CP}$ = 11.2 Hz, *C*S). ^{31}P NMR ($CDCl_3$, δ): 4.61.

Preparation of $Os[C_7H_2O(OMe\text{-}7)(CO_2Et\text{-}4)(Ph\text{-}1)(Ph\text{-}2)](CS)(PPh_3)_2$ (3). Compound **2** (51 mg) was heated under reflux in a solution of benzene (8 mL), ethanol (2 mL), and concentrated aqueous HCl (2 drops) for 60 min. Removal of the solvents and recrystallization of the resulting solid from dichloromethane/ethanol gave pure **3** as blue-green microcrystals (27 mg, 51%), *m*/*z* 1118.25137 and 1120.25210; $C_{60}H_{50}O_4{}^{190}OsP_2S$ and $C_{60}H_{50}O_4{}^{192}OsP_2S$ require 1118.24896 and 1120.25200, respectively. Anal. Calc for $C_{60}H_{50}O_4OsP_2S$: C, 64.39; H, 4.50. Found: C, 64.68; H, 4.77. IR (cm^{-1}): 1689, 1570 ν(CO of CO_2CH_3), 1228 ν(CS). ^{1}H NMR

(18) Maddock S. M.; Rickard C. E. F.; Roper W. R.; Wright L. J. *Organometallics* **1996**, *15*, 1793.

($CDCl_3$, δ): 1.22 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2CH_3$ on C4), 3.24 (s, 3H, OCH_3 on C7), 4.00 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2CH_3$ on C4), 5.89−6.87 (m, 10H, *Ph* on C1 and C2), 6.49 (t, 1H, *H*6, $^4J_{CP}$ = 3.6 Hz), 6.98 (s, 1H, *H*3), 7.19−7.33 and 7.48−7.54 (m, 30H, PPh_3). ^{13}C NMR ($CDCl_3$, δ): 14.6 (s, $CO_2CH_2CH_3$ on C4), 52.6 (s, OCH_3 on C7), 59.0 (s, $CO_2CH_2CH_3$ on C4), 123.5, 124.3, 125.0, 126.6, 129.4, 130.1, 148.7, 159.7 (all s, *Ph* on C1 and C2), C4 and C6 resonances not observed, 127.1 (t′, $^{2,4}J_{CP}$ = 9.3 Hz, *o*-PPh_3), 129.5 (s, *p*-PPh_3), 131.7 (t′, $^{1,3}J_{CP}$ = 49.4 Hz, *i*-PPh_3), 135.4 (t′, $^{3,5}J_{CP}$ = 8.7 Hz, *m*-PPh_3), 137.6 (s, *C*2), 157.8 (s, *C*3), 167.7 (s, CO_2Et on C4), 184.6 (s, *C*7), 195.8 (t, $^2J_{CP}$ = 8.1 Hz, *C*1), 219.0 (t, $^2J_{CP}$ = 11.3 Hz, *C*5), 291.0 (t, $^2J_{CP}$ = 9.9 Hz, *C*S). ^{31}P NMR ($CDCl_3$, δ): 4.53.

Preparation of Os[C_7HO(OMe-7)(Br-6)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$ (4). Pyridinium tribromide (12 mg) in methanol (1.5 mL) was added to a stirred solution of **2** (37.2 mg) in dichloromethane (15 mL). The mixture turned instantly from blue-green to green in color. After stirring for 45 min methanol (5 mL) was added and the product crystallized by removing the dichloromethane under reduced pressure. Metallic green crystals of pure **4** (35 mg, 88%) were collected by filtration and washed with methanol and *n*-hexane. The crystal used for the X-ray structure determination was grown from dichloromethane/*n*-hexane and contained some solvent (see Section 4), *m*/*z* 1184.14351, 1182.13944, 1186.15055; $C_{59}H_{47}{}^{81}BrO_4{}^{190}OsP_2S$, $C_{59}H_{47}{}^{79}BrO_4{}^{192}OsP_2S$, $C_{59}H_{47}{}^{79}BrO_4{}^{190}OsP_2S$, and $C_{59}H_{47}{}^{81}BrO_4{}^{192}OsP_2S$, require 1184.14178, 1184.14686, 1182.14382, and 1186.14481, respectively. Anal. Calc for $C_{59}H_{47}BrO_4OsP_2S$: C, 59.85; H, 4.00. Found: C, 59.90; H, 4.08. IR (cm^{-1}): 1709, 1568 ν(CO of CO_2CH_3), 1244 ν(CS). ^1H NMR ($CDCl_3$, δ): 3.14 (s, 3H, OCH_3 on C7), 3.61 (s, 3H, CO_2CH_3 on C4), 6.18−6.86 (m, 10H, *Ph* on C1 and C2), 6.31 (s, 1H, *H*3), 7.26−7.35 and 7.52−7.55 (m, 30H, PPh_3). No ^{13}C NMR was recorded because of sample instability in solution for extended periods. ^{31}P NMR ($CDCl_3$, δ): 4.59.

Preparation of [Os[C_5H(CH_2CO_2Me-5)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$]CF_3CO_2 (5). No crystalline sample of pure **5** was isolated; however, the compound was formed in situ by addition of 4 drops of trifluoroacetic acid to a $CDCl_3$ solution (0.5 mL) of **2** in an NMR tube. The color changed instantly from blue-green to green. This color change was reversed upon addition of ethanol to the $CDCl_3$ solution, and confirmation that **2** was regenerated was apparent from the ^{31}P NMR spectrum. ^1H NMR spectrum of the green solution ($CDCl_3$, δ): 2.97 (s, 2H, *H*6), 3.77 (s, 3H, OCH_3 on C7), 3.87 (s, 3H, CO_2CH_3 on C4), 6.11−6.98 (m, 10H, *Ph* on C1 and C2), 7.11−7.52 (m, 30H, PPh_3), 8.36 (s, 1H, *H*3). ^{13}C NMR ($CDCl_3$, δ): 52.4 (s, CO_2CH_3 on C4), 52.6 (s, *C*6), 56.1 (s, OCH_3 on C7), 125.7, 126.2, 127.5, 128.9, 129.9, 143.7, 162.8 (all s, *Ph* on C1 and C2), 128.3 (t′, $^{1,3}J_{CP}$ = 53.6 Hz, *i*-PPh_3), 128.5 (t′, $^{3,5}J_{CP}$ = 10.5 Hz, *m*-PPh_3), 131.9 (s, *p*-PPh_3), 134.3 (t′, $^{2,4}J_{CP}$ = 10.0 Hz, *o*-PPh_3), 135.4 (s, *C*4), 148.6 (s, *C*2), 153.6 (s, *C*3), 166.6 (s, CO_2CH_3 on C4), 190.2 (s, *C*7), 243.9 (t, $^2J_{CP}$ = 8.1 Hz, *C*5), 280.3 (t, $^2J_{CP}$ = 4.1 Hz, *C*1), 294.8 (t, $^2J_{CP}$ = 11.6 Hz, *C*S). ^{31}P NMR ($CDCl_3$, δ): 1.04.

Preparation of [Os[C_5H(CH_2CO_2Me-5)(CO_2Me-4)(Ph-1)(Ph-2)](CS)(PPh_3)$_2$]I_3 (6). HI gas (containing I_2 as an impurity) was passed through a solution of compound **2** (22 mg) in CH_2Cl_2 (10 mL) for a period of 3 min. Within the first minute the color changed from blue-green to green. Removal of solvent afforded a green solid, which was recrystallized from CH_2Cl_2/*n*-heptane to give pure **6** as dark green crystals (23 mg, 94%), *m*/*z* 1105.24044 and 1107.24188; $C_{59}H_{49}O_4{}^{190}OsP_2S$ and $C_{59}H_{49}O_4{}^{192}OsP_2S$ require 1105.24114 and 1107.24417, respectively. The crystal for the X-ray structure determination was grown from a mixture of $CDCl_3$/CH_2Cl_2/*n*-heptane and proved to be a 1:1 CH_2Cl_2 solvate (see Table 1), but the bulk sample obtained as above from CH_2Cl_2/*n*-heptane analyzed correctly as a 1:1.5 CH_2Cl_2 solvate. Anal. Calc for $C_{59}H_{49}I_3O_4OsP_2S\cdot1.5CH_2Cl_2$: C, 45.01; H, 3.25. Found: C, 45.02; H, 3.17. IR (cm^{-1}): 1703, 1621 ν(CO of CO_2CH_3), 1258 ν(CS). ^1H NMR spectrum of green solution ($CDCl_3$, δ): 2.94 (s, 2H, *H*6), 3.86 (s, 3H, OCH_3 on C7), 3.93 (s, 3H, CO_2CH_3 on C4), 6.12−6.96 (m, 10H, *Ph* on C1 and C2), 7.13−7.52 (m, 30H, PPh_3), 8.39 (s, 1H, *H*3). ^{13}C NMR ($CDCl_3$, δ): 52.0 (s, CO_2CH_3 on C4), 52.7 (s, *C*6), 58.1 (s, OCH_3 on C7), 125.7, 126.3, 127.4, 128.6, 130.0, 144.2, 162.8 (all s, *Ph* on C1 and C2), 128.3 (t′, $^{1,3}J_{CP}$ = 52.7 Hz, *i*-PPh_3), 128.6 (t′, $^{3,5}J_{CP}$ = 10.5 Hz, *m*-PPh_3), 131.8 (s, *p*-PPh_3), 134.4 (t′, $^{2,4}J_{CP}$ = 10.0 Hz, *o*-PPh_3), 135.7 (s, *C*4), 148.3 (s, *C*2), 153.8 (s, *C*3), 166.7 (s, CO_2CH_3 on C4), 189.8 (s, *C*7), 243.5 (t, $^2J_{CP}$ = 7.9 Hz, *C*5), 279.2 (t, $^2J_{CP}$ = 4.0 Hz, *C*1), 294.4 (t, $^2J_{CP}$ = 11.7 Hz, *C*S). ^{31}P NMR ($CDCl_3$, δ): 1.04.

X-ray Crystal Structure Determination for Complexes 2, 3, 4, and 6. X-ray intensity data were recorded on a Siemens SMART diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 84 K. Data were integrated and corrected for Lorentz and polarization effects using SAINT.[19] Semiempirical absorption corrections were applied based on equivalent reflections using SADABS.[20] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the programs SHELXS97[21] and SHELXL97.[22] For compounds **2**, **3**, and **4** all non-hydrogen atoms were refined anisotropically. Crystals of **4** contain disordered solvent of crystallization, which could not be modeled satisfactorily. An electron count from "solvent squeezing"[23] indicates one molecule of CH_2Cl_2 per molecule of complex in the crystals used for the X-ray structure. The triiodide ion of **6** is disordered over two sites with occupancies refined to 0.884 and 0.126. Each partial triiodide was constrained to be linear with typical I−I bond distances. In a void in the crystal lattice of **6** there were discrete peaks in the difference electron density map that could be resolved into overlapping CH_2Cl_2 and $CHCl_3$ molecules of crystallization. The occupancies were refined to 0.876 for CH_2Cl_2 and 0.124 for $CHCl_3$. Isotropic temperature factors were employed for the minor component of the triiodide ion and the carbons of the disordered solvent molecules; all other non-hydrogen atoms of **6** were refined anisotropically. Hydrogen atoms for all structures were located geometrically and refined using a riding model. Diagrams were produced using ORTEP3.[2424]

Acknowledgment. We thank the Marsden Fund administered by the Royal Society of NZ for supporting this work and for the award of a Ph.D. scholarship to P.M.J.

Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **2**, **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0510371

(19) Siemens. *SMART* and *SAINT*; Siemens Analytical Instruments Inc.: Madison, WI, 1995.

(20) Sheldrick G. M. *SADABS, Program for semiempirical absorption correction*; University of Göttingen: Göttingen, Germany, 1997.

(21) Sheldrick G. M. *SHELXS, Program for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1977.

(22) Sheldrick G. M. *SHELXL, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

(23) Van der Sluis P.; Spek A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(24) Burnett M. N.; Johnson C. K. *ORTEP-III*: *Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*; Oak Ridge National Laboratory report ORNL-6895; 1996.