4964 *Organometallics* **2004,** *23,* 4964−4969

η^1-Bound 2-Pyrone Complexes of Molybdenum and Iron: A Synthetic and Structural Study

Ian J. S. Fairlamb, Jason M. Lynam,* Ian E. Taylor, and Adrian C. Whitwood

Department of Chemistry, University of York, Heslington, York, U.K. YO10 5DD

Received June 30, 2004

Oxidative cleavage of the $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ with $AgBF_4$ in the presence of 4-methoxy-6-methyl-2-pyrone or 3-bromo-4-methoxy-6-methyl-2-pyrone results in the formation of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}H\}][BF_4]$ and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}Br\}][BF_4]$, respectively. Single-crystal X-ray diffraction studies have demonstrated that the orientation of the 2-pyrone ligands varies markedly within the two complexes. In the case of the 4-methoxy-6-methyl-2-pyrone complex the pyrone unit lies parallel to the Mo−CO axis, whereas the bromo-substituted pyrone lies in a perpendicular orientation. Similarly, reactions of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with $AgBF_4$ in the presence of 4-methoxy-6-methyl-2-pyrone or 3-bromo-4-methoxy-6-methyl-2-pyrone result in formation of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}\overline{COCMe{=}CHC(OMe){=}C}H\}][BF_4]$ and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}\overline{COCMe{=}CHC(OMe){=}C}Br\}][BF_4]$, respectively. Whereas the orientations of the pyrone ligands in the molybdenum and iron complexes containing the brominated 2-pyrone ligands are identical, the iron complex containing the 4-methoxy-6-methyl-2-pyrone contains three cations in the asymmetric unit, two of which have the 2-pyrone ligand perpendicular to the Cp(centroid)−Fe axis, whereas the third unit is parallel. The 2-pyrone ligands of these cations form a stack in which the parallel unit is sandwiched between the two with a perpendicular orientation. The pyrone ligands appear to be only weakly coordinated to the metals and solutions of the complexes rapidly decompose. The complex $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}H\}][BF_4]$ reacts with $PhC{\equiv}CPh$ to give $[Mo(CO)(\eta^2\text{-}PhC{\equiv}CPh)_2(\eta^5\text{-}C_5H_5)][BF_4]$.

Introduction

The 2-pyrone ring system is a fundamentally important unit in terms of its structure and reactivity.[1] Our interest in this system derives from the fact that it is a common building block in nature and is found in many biological systems.[2] More recently we (I.J.S.F.) have shown that 4-alkynyl-6-methyl-2-pyrones (**1**), as well as the related 4-alkenyl- and 4-aryl-6-methyl-2-pyrones, inhibit the growth of A2780 human ovarian carcinoma and K5762 human chronic myelogenous leukemia cell lines at the sub-micromolar level.[3] Such promising inhibitory activity has prompted our efforts to study the chemistry of various functionalized 2-pyrones.

It is well-known that coordination of organic molecules to metal fragments may have a pronounced effect on their structure and reactivity,[4] and as part of a continued program focusing on the exploitation of palladium-catalyzed carbon−carbon and carbon−heteroatom bond-forming reactions in the synthesis of novel 2-pyrones,[3] we wished to utilize this phenomenon. For example, we have shown that reaction of 4-bromo-6-methyl-2-pyrone (**2**) with Grevels' reagent $[Fe(coe)_2(CO)_3]$ (coe = *cis*-cyclooctene) resulted in the formation of $Fe(CO)_3$(4-bromo-6-methyl-η^4-2-pyrone) (**3**), in which the 2-pyrone unit is bound to the iron in an η^4-diene-like fashion.[5] Crucially, coordination of the 2-pyrone to the iron tricarbonyl fragment activates the bromine substituent for Suzuki−Miyaura cross-coupling reactions, in comparison to the free 2-pyrone, **2**.

Although this chemistry illustrated the potential power of our approach, there are some synthetic difficulties in employing Grevels' reagent, which has to be

---

(1) (a) Vardaro, R. R.; DiMarzo, V.; Crispino, A.; Cimino, G. *Tetrahedron* **1991**, *47*, 5569. (b) Groutas, W. C.; Stanga, M. A.; Brubaker, M. J.; Huang, T. L.; Moi, M. K.; Carroll, R. T. *J. Med. Chem.* **1985**, *28*, 1106.

(2) Dickinson, J. M. *Nat. Prod. Rep.* **1993**, *10*, 71.

(3) (a) Marrison, L. R.; Dickinson, J. M.; Fairlamb, I. J. S. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3509. (b) Marrison, L. R.; Dickinson, J. M.; Ahmed, R.; Fairlamb, I. J. S. *Tetrahedron Lett.* **2002**, *43*, 8853. (c) Marrison, L. R.; Dickinson, J. M.; Ahmed, R.; Fairlamb, I. J. S. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 2667. (d) Fairlamb, I. J. S.; Lu, F.-J.; Schmidt, J.-P. *Synthesis* **2003**, 2564. (e) Fairlamb, I. J. S.; Bäuerlein, P. S.; Marrison, L. R.; Dickinson, J. M. *Chem. Commun.* **2003**, 632.

(4) See, for example: *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12 (Hegedus, L. S., Vol. Ed.).

(5) (a) Fairlamb, I. J. S.; Syvänne, S. M.; Whitwood, A. C. *Synlett* **2003**, 1693. For other metal pyrone carbonyl complexes, see: (b) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363. (c) Mitsudo, T.; Watanabe, Y.; Nakanishi, H.; Morishima, I.; Inubushi, T.; Takegami, Y. *J. Chem. Soc., Dalton Trans.* **1978**, 1298. (d) Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368. (e) Mitsudo, T.-A.; Watanabe, H.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Kafuku, K.; Kinoshita, K.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1981**, 22.

10.1021/om049523w CCC: $27.50

prepared by photolysis at low temperature (<−40 °C) from $Fe(CO)_5$ and *cis*-cyclooctene in hexane.[6] When it is warmed to >−40 °C, Grevels' reagent rapidly decomposes.[6,7] This has made it difficult to apply this route to the large-scale synthesis of **3**. We therefore wished to expand the range of metal fragments that will coordinate to the 2-pyrone unit, with a particular emphasis placed upon developing a large-scale, high-yielding synthesis of the resulting complexes.

Herein, we describe the synthesis of 2-pyrone complexes of both molybdenum and iron. Although our intention was to prepare complexes with the 2-pyrone bound in an η^4-diene fashion, we have discovered a general route for complexation of the 2-pyrone unit bound in an η^1-fashion, through the oxygen of the carbonyl function. To the best of our knowledge, this represents a new binding mode to metals for this unusual ligand.

Results and Discussion

Our initial attempts to synthesize molybdenum complexes containing a 2-pyrone ligand focused on the use of $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_5H_5)][BF_4]$ (**4**) as a molybdenum transfer agent. It is well established that **4** and its analogues may act as versatile precursors for a range of η^4-bound diene and diene-like[8] complexes, and we therefore reasoned that reaction of **4** with a 2-pyrone should, in a manner similar to that for the iron complexes **3**, result in coordination of the organic ligand in an η^4 fashion. Given the successful exploitation of the $[Mo(CO)_2(\eta^5\text{-}L)]$ ($L = C_5H_5, C_5Me_5, C_9H_7$, Tp) fragment in developing the chemistry of coordinated organic ligands,[9] we reasoned that molybdenum complexes containing η^4-bound 2-pyrone ligands may also exhibit a rich chemistry.

Treatment of dichloromethane solutions of **4** with a variety of substituted and unsubstituted 2-pyrones did not, however, lead to the formation of any new product. When these solutions were heated at reflux for several hours, new bands in the CO stretching region were occasionally observed in their IR spectra. In all cases, however, the bands rapidly disappeared on cooling the solution to room temperature. This led us to conclude that, at high temperature, the 2-pyrone was coordinated to some extent to the metal; presumably, on cooling, the acetonitrile that was liberated during this process simply displaced the coordinated 2-pyrone to regenerate **4**. It was therefore clear that a different protocol would be required to produce molybdenum 2-pyrone complexes.

Oxidation of the dimeric complex $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (**5**) with $AgBF_4$ in the presence of substrates such as alkenes, dienes, alkynes, and phosphines has also been shown to be an useful procedure to facilitate the incorporation of organic groups into the coordination sphere of the metal.[8a,10] Treatment of a dichloromethane solution of **5** with 2 equiv of $AgBF_4$ and an excess of 4-methoxy-6-methyl-2-pyrone (**6**) resulted, after 16 h, in complete conversion to the single product **7**, as shown by IR spectroscopy. NMR spectra of **7** in CD_2Cl_2 solution demonstrated that a selective reaction had occurred but that the 2-pyrone ligand was not coordinated in an η^4 fashion. For example, the carbon atoms of the 2-pyrone framework all exhibited extremely small coordination shifts in the ^{13}C NMR spectrum and two resonances were observed in the metal carbonyl region at δ 227.7 and 237.8. The IR spectra of the reaction mixture indicated that a selective reaction had occurred, as two new peaks were observed in the M−CO stretching region at 2067 and 1983 cm^{-1} and the pattern of the two bands was consistent with the presence of a $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ fragment. Furthermore, two new bands were observed in the region characteristic of the 2-pyrone group at 1670 and 1552 cm^{-1}. Considering that the C═O stretch for the free 2-pyrone unit is observed above 1700 cm^{-1}, this shift in frequency led us to believe that the pyrone unit was bound to the metal though its carbonyl oxygen.

This hypothesis was confirmed by a single-crystal X-ray diffraction study. Single crystals of **7**, suitable for study by X-ray diffraction, were grown by slow diffusion of diethyl ether into a dichloromethane solution of **7** that also contained some uncoordinated 4-methoxy-6-methyl-2-pyrone (**6**): the resulting structure is shown in Figure 1. The cation of **7** adopts a distorted four-legged piano-stool geometry with the molybdenum being bound to a cyclopentadienyl ligand, three carbonyls, and, as predicted on the basis of the IR spectra, a carbonyl-oxygen-bound 4-methoxy-6-methyl-2-pyrone unit. The bond lengths within the 2-pyrone unit are remarkably unperturbed on binding to the metal and show no major statistically significant differences from the free 2-pyrone:[11] the Mo−O distance is 2.163(2) Å. The carbonyl

---

[6] Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

[7] Knölker, H.-J.; Baum, G.; Foitzik, N.; Goesmann, H.; Gonser, P.; Jones, P. G.; Röttele, H. *Eur. J. Inorg. Chem.* **1998**, 993 and references therein.

[8] (a) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365. (b) Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18. (c) Baxter, J. S.; Green, M.; Lee, T. V. *J. Chem. Soc., Chem. Commun.* **1989**, 1595. (d) Benyunes, S. A.; Binelli, A.; Green, M.; Grimshire, M. J. *J. Chem. Soc., Dalton Trans.* **1991**, 895. (e) Butters, C.; Carr, N.; Deeth, R. J.; Green, M.; Green, S. M.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **1996**, 2299. (f) Beddows, C. J.; Box, M. R.; Butters, C.; Carr, N.; Green, M.; Kursawe, M.; Mahon, M. F. *J. Organomet. Chem.* **1998**, *555*, 267.

[9] (a) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660. (b) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736. (c) Rubio, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 891. (d) Yu, R. H.; McCallum, S.; Liebeskind, L. S. *Organometallics* **1994**, *13*, 1476. (e) Benyunes, S. A.; Deeth, R. J.; Fries, A.; Green, M.; McPartlin, M.; Nation, C. B. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3453. (f) Ward, Y. D.; Villanuvea, L. A.; Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 897. (g) Pearson, A. J.; Douglas, A. R. *Organometallics* **1998**, *17*, 1446. (h) Yin, J.; Llorente, I.; Villanueva, L. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2000**, *121*, 10458. (i) Moretto, A. F.; Liebeskind, L. S. *J. Org. Chem.* **2000**, *65*, 7445. (j) Shu, C.; Alcudia, A.; Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 12477. (k) Alcudia, A.; Arrayas, R. G.; Liebeskind, L. S. *J. Org. Chem.* **2002**, *67*, 5773. (l) Shu, C.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 2879. (m) Arrayás, R. G.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2003**, *125*, 9026. (n) Pearson, A. J.; Khan, Md. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748 and references within.

[10] (a) Barnes, S. G.; Green, M. *J. Chem. Soc., Chem. Commun.* **1980**, 267. (b) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1981**, 873. (c) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (d) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319. (e) Kegley, S. E.; Bergstom, D. T.; Crocker, L. S.; Weiss, E. P.; Berndt, W. G.; Rheingold, A. L. *Organometallics* **1991**, *10*, 567. (f) Louattani, E.; Suades, J. *J. Organomet. Chem.* **2000**, *604*, 234.

[11] The X-ray crystal structure of **6** has only been reported as a hydrogen-bonded dimer with succinimide; see: Obata, T.; Shimo, T.; Yoshimoto, S.; Somekawa, K.; Kawaminami, M. *Chem. Lett.* **1999**, *28*, 181.

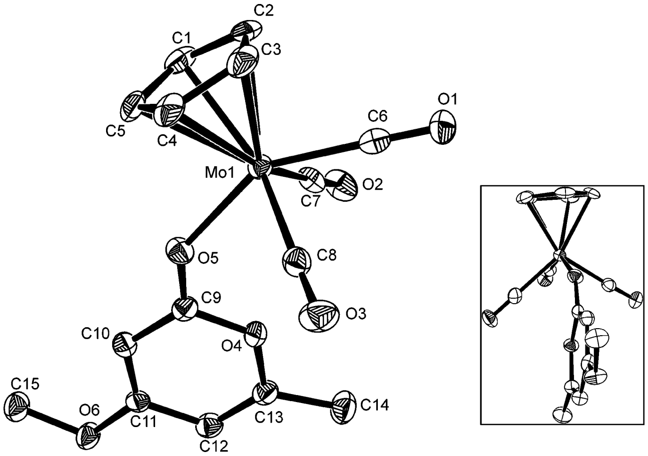

Figure 1. Solid-state structure of the cation of complex **7**. Thermal ellipsoids are shown at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−$Cp_{average}$ = 2.320(3), Mo(1)−C(2) = 2.283(3), Mo(1)−C(3) = 2.275(3), Mo(1)−C(4) = 2.335(3), Mo(1)−C(5) = 2.372(3), Mo(1)−C(6) = 1.982(3), Mo(1)−C(8) = 2.024(3), Mo(1)−C(7) = 2.037(3), Mo(1)−O(5) = 2.163(2), O(5)−C(9) = 1.237(3), O(4)−C(9) = 1.362(3), O(4)−C(13) = 1.378(3), C(13)−C(12) = 1.333(4), C(12)−C(11) = 1.424(4), C(10)−C(11) = 1.364(4); C(6)−Mo(1)−C(8) = 77.01(12), C(6)−Mo(1)−C(7) = 75.71(13), C(8)−Mo(1)−C(7) = 106.85(13), C(6)−Mo(1)−O(5) = 145.92(10), C(8)−Mo(1)−O(5) = 83.14(11), C(7)−Mo(1)−O(5) = 84.08(10), C(9)−O(5)−Mo(1) = 137.02(19). The orientation of the 2-pyrone ligand with respect to the other ligands is shown in the insert.

ligand, which is in a transoid position to the 2-pyrone, shows a shorter Mo−C bond and longer C−O bond compared to the two other, mutually trans, carbonyl ligands.

Given the success of this reaction, we decided to investigate the range of 2-pyrones that could be coordinated to the molybdenum in this fashion. Reaction of a dichloromethane solution of **5** with 2 equiv of $AgBF_4$ and 2-pyrone (**8**) or 4-hydroxy-6-phenyl-2-pyrone (**9**) did not afford complexes analogous to **7**. However, a reaction with 3-bromo-4-methoxy-6-methyl-2-pyrone (**10**) was more successful, affording $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}Br\}][BF_4]$ (**11**). This species was also characterized by NMR and IR spectroscopy, and the structure was confirmed by a single-crystal X-ray diffraction study (Figure 2). Interestingly, the structures of **7** and **11** show a marked difference in the orientation of the 2-pyrone ligands. The $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^+$ units in both complexes are almost identical, but the 4-methoxy-6-methyl-2-pyrone group in **7** lies essentially parallel to the Mo−Cp(centroid)−CO axis (C−Mo−O−C torsion angle 11.2°), whereas in the case of **11** the 2-pyrone is considerably twisted out of this plane (C−Mo−O−C torsion angle 106.5°). One possible explanation for this difference is that the steric bulk of the bromine atom makes the parallel conformation unfavorable.

Having shown that it is possible to prepare molybdenum complexes of the type $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-2-pyrone}\}][BF_4]$ by oxidative cleavage of **5**, we then wished to expand our methodology to include other metals. One obvious choice for this expansion would be to utilize the readily available complex $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (**12**) as a precursor, as it is well established that **12** may undergo oxidative cleavage in the presence of a suitable donor ligand to give complexes analogous to **7** and **11**.[12] Indeed, reaction of **12** with $AgBF_4$ in the presence of excess 4-methoxy-6-methyl-2-pyrone and 3-bromo-4-methoxy-6-methyl-2-pyrone afforded $[Fe(CO)_2(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}H\}][BF_4]$ (**13**) and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}O{=}\overline{COCMe{=}CHC(OMe){=}C}Br\}][BF_4]$ (**14**), respectively: both species were characterized by NMR and IR spectroscopy, as well as by single-crystal X-ray diffraction.

The solid-state structure of complex **14** (Figure 3) was of particular interest, as again the 3-bromo-4-methoxy-6-methyl-2-pyrone unit adopted a geometry akin to that seen in **11**; viz., the 2-pyrone unit is lying almost perpendicular to the $Cp_{centroid}$−Fe−O plane (torsion angle 96.0°). The structure of **13** was somewhat more curious, however. Crystals were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **13**. The asymmetric unit of the resulting structure contains three iron cations and three BF_4 anions, and there are no statistically significant differences within the bond lengths within these three iron units; however, the orientation of the 2-pyrone ligands does vary with respect to these iron centers. In two of the iron centers the 2-pyrone is lying in a position perpendicular to the Fe−$Cp_{centroid}$ axis (torsion angle $Cp_{centroid}$−Fe−O−C = 93.4°), as in complexes **11** and **14**, but the 2-pyrone in the remaining (central) iron unit is parallel, with the $Cp_{centroid}$ axis (torsion angle $Cp_{centroid}$−Fe−O−C = 171.3°). If one just considers the cationic Fe units in the crystal structure, there is essentially a mirror plane running through the 2-pyrone attached to the central iron. The 2-pyrone units in the three iron complexes therefore form a stack, as shown in Figure 4. It is not clear whether this is a result of $\pi-\pi$ interactions through neighboring 2-pyrone units (the closest contact between neighboring 2-pyrones is 3.254 Å) or as a result of crystal packing forces. In this complex at least, there must be an extremely small difference in energy between a perpendicular and parallel orientation of the 2-pyrone ligand.

A search of the Cambridge Structural Database[13] revealed that only two structures containing the "$Mo(CO)_3(\eta^5\text{-}C_5H_5)L$" fragment, where L is an oxygen-bound donor ligand, have been characterized by X-ray diffraction methods. Beck and co-workers have prepared $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}COCH_3\}Fe(CO)_2(\eta^5\text{-}C_5H_5)][SbF_6]$—here the iron acyl binds to the molybdenum center and the Mo−O(acyl) bond length is 2.158(8) Å, analogous to that observed in complexes **7** and **11**.[14] Furthermore, the acyl unit adopts an arrangement of the 2-pyrone unit similar to that in complex **7**: i.e., it lies essentially

---

[12] (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Williams, W. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1329. (c) Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307. (d) Cicero, R. L.; Protasiewicz, J. D. *Organometallics* **1995**, *14*, 4792. (e) Schumann, H.; Speis, M.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T. *J. Organomet. Chem.* **1991**, *403*, 165. (f) Schumann, H.; Eguren, L. *J. Organomet. Chem.* **1991**, *403*, 183.

[13] Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388.

[14] Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227.

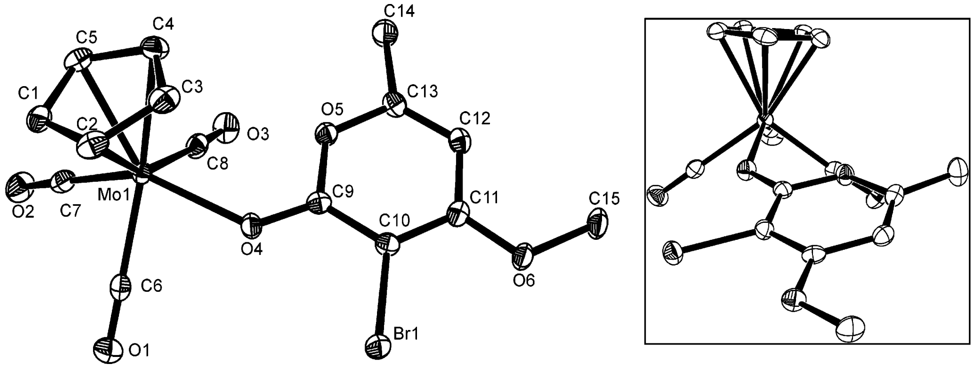

Figure 2. Solid-state structure of the cation of complex **11**. Thermal ellipsoids are shown at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)–$Cp_{average}$ = 2.325(2), Mo(1)–C(1) = 2.284(2), Mo(1)–C(2) = 2.347(2), Mo(1)–C(3) = 2.381(2), Mo(1)–C(4) = 2.338(2), Mo(1)–C(5) = 2.277(2), Mo(1)–C(6) = 2.043(3), Mo(1)–C(7) = 2.006(2), Mo(1)–C(8) = 2.011(2), Mo(1)–O(4) = 2.1979(14), O(4)–C(9) = 1.248(3), Br(1)–C(10) = 1.874(2), O(5)–C(9) = 1.351(3), O(5)–C(13) = 1.363(3), C(8)–O(3) = 1.141(3), C(12)–C(13) = 1.341(3), C(12)–C(11) = 1.420(3), C(9)–C(10) = 1.410(3); C(7)–Mo(1)–C(8) = 79.03(9), C(7)–Mo(1)–C(6) = 76.15(9), C(8)–Mo(1)–C(6) = 107.40(9), C(7)–Mo(1)–O(4) = 142.95(8), C(8)–Mo(1)–O(4) = 85.75(7), C(6)–Mo(1)–O(4) = 76.57(7), C(9)–O(4)–Mo(1) = 130.95(14). The orientation of the 2-pyrone ligand with respect to the other ligands is shown in the insert.

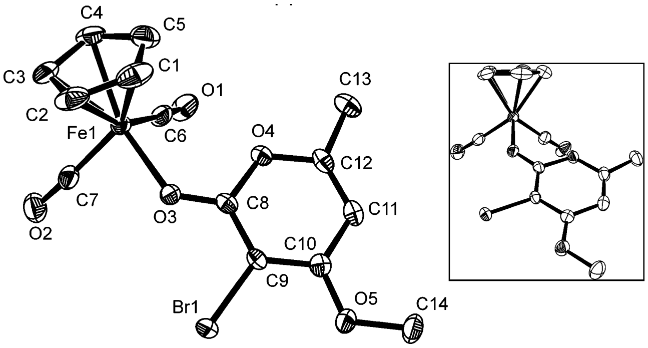

Figure 3. Solid-state structure of the cation of complex **14**. Thermal ellipsoids are shown at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–$Cp_{average}$ = 2.089(2), Fe(1)–C(1) = 2.122(2), Fe(1)–C(2) = 2.083(2), Fe(1)–C(3) = 2.067(2), Fe(1)–C(4) = 2.069(2), Fe(1)–C(5) = 2.103(2), Fe(1)–O(3) = 1.9857(14), Fe(1)–C(6) = 1.801(2), Fe(1)–C(7) = 1.808(2), Br(1)–C(9) = 1.8733(17), O(3)–C(8) = 1.240(2), O(4)–C(8) = 1.369(2), O(4)–C(12) = 1.367(2), C(11)–C(12) = 1.347(3), C(11)–C(10) = 1.425(3), C(9)–C(10) = 1.381(3), C(9)–C(8) = 1.398(3); C(6)–Fe(1)–C(7) = 93.65(10), C(6)–Fe(1)–O(3) = 97.55(7), C(7)–Fe(1)–O(3) = 90.61(8), C(6)–Fe(1)–C(3) = 125.52(9), C(8)–O(3)–Fe(1) = 130.50(12). The orientation of the 2-pyrone ligand with respect to the other ligands is shown in the insert.

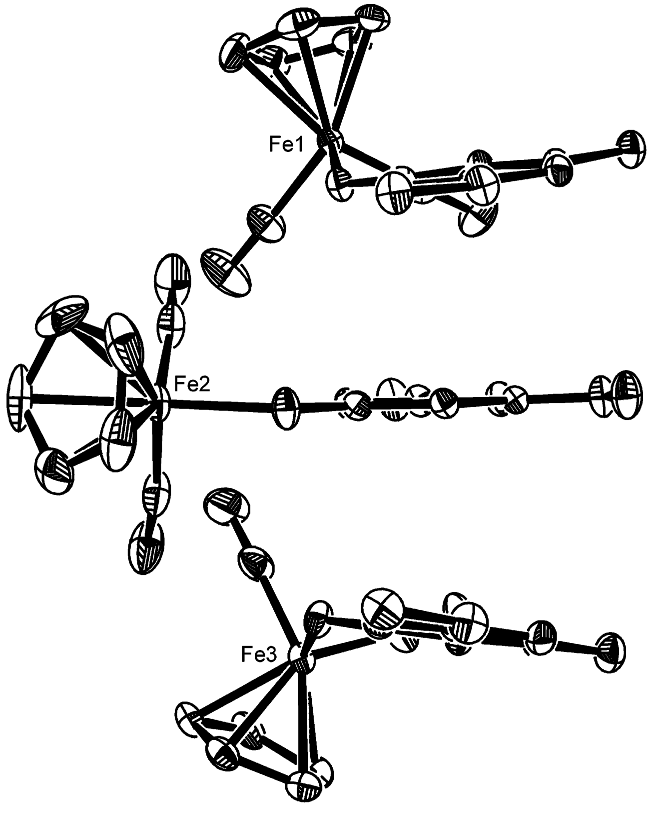

Figure 4. Structure of the cations of complex **13** in the solid state. Thermal ellipsoids are shown at the 50% probability level, and all hydrogen atoms are omitted for clarity.

parallel to the Mo–$Cp_{centroid}$–CO axis. Also, the complex $[Mo(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^1(O)\text{-}SO_3CF_3\}]$ has been prepared by Lindner and co-workers and shows a Mo–O bond length of 2.212(2) Å.[15] The difference in Mo–O bond length may simply be due to the fact that the cationic charge in complexes **7** and **11** makes the molybdenum a better Lewis acid.

There is slightly more information available, however, for the solid-state structures of complexes $[Fe(CO)_2(\eta^5\text{-}C_5H_5)L][BF_4]$, where L is an η^1-oxygen-bound donor atom. In the cases where L = tropone,[16] nitrobenzene,[17] *p*-chlorobenzaldehyde, *p*-anisaldehyde,[12d] the ligand adopts an orientation similar to that seen in complex **7**, whereas in the case where L = cyclohexenone the geometry is similar to that of **11**.[12a] Very recently, the complex $[Fe(CO)_2(\eta^5\text{-}C_5Me_5)\{\eta^1(O)\text{-}O{=}CPh_2\}][BAr^f_4]$ (Ar^f = $C_6H_3(CF_3)_2$-3,5) has been prepared in the remarkable reaction between $[Fe(CO)_2(\eta^5\text{-}C_5Me_5)({=}BMes)][BAr^f_4]$ and benzophenone.[18] Here the benzophenone ligand adopts a geometry similar to that of the 2-pyrone in **11**. The bond lengths between the iron and the oxygen of

---

(15) Lindner, E.; Henes, M.; Wielandt, W.; Eichele, K.; Steimann, M.; Luinstra, G. A.; Görtz, H.-H. *J. Organomet. Chem.* **2003**, *681*, 12.

(16) Boudjouk, P.; Woell, J. B.; Radonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 582.

(17) Srivastava, R. S.; Khan, M. A.; Nicholas, K. M. *Inorg. Chim. Acta* **2003**, *349*, 269.

(18) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911.

the 2-pyrone ligands are Fe(1)−O(3) = 1.9857(14) Å for complex **14** and an average of 1.9808 Å for the three units in complex **13** and is typical for the above complexes. In accordance with our observations for the η^1-oxygen-bound 2-pyrone complexes, coordination of these ligands to the iron center does not result in any major deviations in the bond lengths of the ligand skeleton. Indeed, the bond lengths within the coordinated 2-pyrone fragments to either molybdenum or iron are all remarkably similar.

It should be noted that all of the metal-bound 2-pyrone complexes decompose over a period of a few hours at room temperature in solution to give insoluble materials (thought to be either molybdenum or iron metal) and the uncoordinated 2-pyrone. We have not obtained any evidence for dehydrobromination reactions, as in the case of similar reaction with Grevels' reagent.[5] This led us to believe that these species could act as precursors for compounds containing $[M(CO)_x(\eta^5\text{-}C_5H_5)]^+$ units (M = Mo, $x = 3$; M = Fe, $x = 2$). In a preliminary study, we have shown that complex **7** does indeed act in a manner analogous to other sources of the $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^+$ unit: viz., reaction of **7** with PhC≡CPh resulted in quantitative conversion (as shown by IR spectroscopy) to $[Mo(CO)(\eta^2\text{-}PhC{\equiv}CPh)_2(\eta^5\text{-}C_5H_5)]$ (**15**). The fact that the 2-pyrones appear to be labile is also consistent with our initial findings in the $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_5H_5)][BF_4]$ system. Presumably in this case, on heating to reflux in the presence of 2-pyrone, $[Mo(CO)_2(NCMe)\{\eta^1(O)\text{-2-pyrone}\}(\eta^5\text{-}C_5H_5)]^+$ and NCMe are formed, which on cooling regenerates **4** and free 2-pyrone.

We are currently exploring the range of 2-pyrones, as well as other substituted oxygen- and nitrogen-containing heterocycles that may be coordinated to molybdenum and iron in this fashion. Parallel with these studies, we are also examining the reactivity of the new molybdenum and iron complexes with a view to exploring novel derivatizations of the 2-pyrone ring system.

Experimental Section

All reactions were performed under an atmosphere of nitrogen using standard Schlenk-line techniques. Solvents were purified and dried using appropriate drying agents and distilled under argon prior to use. $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$[19] and $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$[20] were prepared using established procedures. $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_5H_5)]BF_4$ was prepared by a modification of the method reported by Green and co-workers.[8e] 4-Hydroxy-6-methyl-2-pyrone (**9**) and the parent pyrone **8** were purchased from Lancaster and Fluka, respectively, and used as supplied. 4-Methoxy-6-methyl-2-pyrone (**6**) and 3-bromo-4-methoxy-6-methyl-2-pyrone (**10**) were prepared using a literature procedure.[21] $AgBF_4$ was purchased from Fluorochem and used as supplied.

NMR spectra were acquired on a Bruker AMX500 spectrometer (operating frequencies: ^{1}H, 500.1 MHz; ^{13}C, 125.7 MHz). All NMR spectra were acquired in CD_2Cl_2 solution at 300 K, and assignments were confirmed with the aid of ^{13}C DEPT 135, ^{1}H−^{1}H COSY, ^{1}H−^{1}H NOESY, and ^{1}H−^{13}C HMQC experiments. IR spectra were acquired in CH_2Cl_2 solution using a Mattson Research Series FTIR spectrometer and CsCl solution cells. Fast atom bombardment (FAB) mass spectrometry measurements were performed by Dr. T. A. Dransfield and Mr. B. R. Glennie using a Fisons analytical (VG) Autospec instrument.

Preparation of $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_5H_5)]BF_4$. To a purple CH_3CN (20 mL) solution of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (1 g, 2.04 mmol) was added $AgBF_4$ (0.825 g, 4.10 mmol). The reaction flask was shielded from the light with aluminum foil and then heated at reflux under an atmosphere of N_2. The reaction was monitored by IR spectroscopy. After 16 h the mixture had changed color to yellow-brown and the IR spectrum showed that no starting material remained. After filtration through Celite all of the volatile materials were removed in vacuo. Recrystallization of the residue from CH_2Cl_2/ether at −20 °C yielded light brown crystals after filtration: further batches of the product were obtained by storing the mother liquor at −20 °C. Yield: 0.675 g (86%). ^{1}H NMR (δ): 5.72 (s, 5H, C_5H_5), 2.52 (s, 6H, $CNCH_3$). IR (CH_2Cl_2; cm^{-1}): 1997 (ν(CO)), 1913 (ν(CO)).

Preparation of 7. To a stirred CH_2Cl_2 solution of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (100 mg, 0.20 mmol), shielded from the light by aluminum foil, were added 4-methoxy-6-methyl-2-pyrone (114 mg, 0.81 mmol) and $AgBF_4$ (79 mg, 0.41 mmol). The onset of reaction was indicated by the precipitation of silver metal in the flask. Stirring was continued until an infrared spectrum of an aliquot of the reaction mixture indicated that no $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ remained. This typically took 16 h. The reaction mixture was then filtered, the volume of CH_2Cl_2 was reduced to approximately 2 mL in vacuo, and diethyl ether (10 mL) was added, causing the product to precipitate as an orange-red powder. The powder was washed with diethyl ether and dried in vacuo. If crystals of the product were required, the reaction was performed as described above; however, the product was not precipitated directly from solution. In this case an overlayer of diethyl ether was placed on the CH_2Cl_2 solution containing **3** and excess 4-methoxy-6-methyl-2-pyrone. Slow diffusion of diethyl ether into this solution afforded crystals suitable for study by single-crystal X-ray diffraction, although some decomposition did occur to give a metallic residue, which was assumed to be molybdenum. Attempts to crystallize the complex in the absence of excess 4-methoxy-6-methyl-2-pyrone resulted in total decomposition. Yield: 35 mg (36%). ^{1}H NMR (δ): 6.27 (s, 1H, $=CH$), 5.95 (s, 5H, C_5H_5), 5.93 (s, 1H, $=CH$), 3.92 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (δ): 237.8 (s, M−CO), 227.7 (s, M−CO), 174.6 (s), 174.4 (s), 164.4 (s), 103.9 (s, CH of 2-pyrone), 97.2 (s, C_5H_5), 90.5 (s, CH of 2-pyrone), 57.4 (s, OCH_3), 18.9 (s, CH_3). MS FAB$^+$ (m/z): 387 M$^+$, correct isotopic distribution for $C_{15}H_{13}O_6Mo$; fragment peak at 359 (M − CO)$^+$. IR (CH_2Cl_2 solution, CsCl plates; cm^{-1}): 2067 (ν(CO)), 1983 (ν(CO)), 1670 (C=O), 1552 (pyrone backbone).

Preparation of 11. Complex **11** was prepared in a fashion similar to **7** from $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (28 mg, 0.06 mmol) and $AgBF_4$ (22 mg, 0.11 mmol): 3-bromo-4-methoxy-6-methyl-2-pyrone (50 mg, 0.23 mmol) was used in place of 4-methoxy-6-methyl-2-pyrone. ^{1}H NMR (δ): 6.76 (s, 1H, $=CH$), 5.95 (s, 5H, C_5H_5), 4.11 (s, 3H, OCH_3), 2.52 (s, 3H, CH_3). ^{13}C NMR (δ): 237.3 (s, M−CO), 227.3 (s, M−CO), 171.1 (s), 170.1 (s), 166.1 (s), 99.5 (s, CH of 2-pyrone), 97.2 (s, C_5H_5), 90.8 (s, CBr), 58.4 (s, OCH_3), 19.3 (s, CH_3). MS FAB$^+$ (m/z): 465 M$^+$, correct isotopic distribution for $C_{15}H_{12}BrO_6Mo$; fragment peaks at 437 (M − CO)$^+$, 400 (M − C_5H_5)$^+$, 381 (M − 3CO)$^+$. IR (CH_2Cl_2 solution, CsCl plates; cm^{-1}): 2068 (ν(CO)), 1986 (ν(CO)), 1658 (C=O), 1511 (pyrone backbone).

Preparation of 13. Complex **13** was prepared in a fashion similar to that for **7**, with the exception that $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (100 mg, 0.28 mmol) was used in place of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$: $AgBF_4$ (109 mg, 0.56 mmol) and 4-methoxy-6-

---

[19] Manning, A. R.; Hackett, P.; Birdwhistell, R.; Soye, R. *Inorg. Synth.* **1990**, *28*, 148. The $Na[C_5H_5]$ used in this reaction was prepared by the method described by Roesky. See: Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2003**, *22*, 877.

[20] King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *12*, 110.

[21] (a) de March, P.; Moreno-Mañas, M.; Pi, R.; Ripoll, I.; Sánchez-Fernando, F. *J. Heterocycl. Chem.* **1985**, *22*, 1537. (b) De March, P.; Moreno-Mañas, M.; Ripoll, I. *Synth. Commun.* **1984**, *14*, 521.

Table 1. Crystallographic Data for New Complexes

	7	**11**	**13**	**14**
formula	$C_{15}H_{13}BF_4MoO_6$	$C_{15}H_{12}BBrF_4MoO_6$	$C_{14}H_{13}BF_4FeO_5$	$C_{14}H_{12}BBrF_4FeO_5$
M_r	472.00	550.91	403.90	482.81
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$
a/Å	11.8131(11)	7.6608(4)	10.4420(6)	6.6123(4)
b/Å	11.8309(11)	24.8663(13)	12.3557(7)	12.2114(7)
c/Å	12.6976(12)	9.9833(6)	20.6549(11)	21.4058(12)
α/deg	90	90	75.425(1)	90
β/deg	98.661(2)	100.445(1)	77.074(1)	90
γ/deg	90	90	72.982(1)	90
V/Å^3	1754.4(3)	1870.26(18)	2433.5(2)	1728.42(17)
Z	4	4	6	4
μ/mm^{-1}	0.818	2.906	0.995	3.248
no. of rflns collected	9741	12792	17010	13710
no. of indep rflns	3091	4291	11113	4989
goodness of fit on F^2	0.979	1.025	1.026	0.962
final R indices ($I > 2\sigma(I)$): R1, wR2	0.0278, 0.0511	0.0244, 0.0548	0.0430, 0.1019	0.0230, 0.0465

methyl-2-pyrone (158 mg, 1.08 mmol) were added as described above. Yield: 112 mg (49%). ^{1}H NMR (δ): 6.17 (s, 1H, $=$CH), 5.33 (s, 5H, C_5H_5), 5.76 (s, 1H, $=$CH), 3.85 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR (δ): 210.2 (s, M$-$$C$O), 174.2 (s), 173.2 (s), 163.3 (s), 103.4 (s, CH of 2-pyrone), 90.5 (s, CH of 2-pyrone), 85.7 (s, C_5H_5), 57.1 (s, OCH$_3$), 18.7 (s, CH$_3$). MS FAB$^+$ (m/z): 317 M$^+$; fragment ion peaks at 261 (M $-$ 2 CO)$^+$. IR (CH_2Cl_2 solution, CsCl plates; cm^{-1}): 2068 (ν(CO)), 2022 (ν(CO)), 1676 (C$=$O), 1556 (pyrone backbone).

Preparation of 14. Complex **14** was prepared in a fashion similar to that for **7** from [Fe(CO)$_2$(η^5-C_5H_5)]$_2$ (50 mg, 0.14 mmol), $AgBF_4$ (55 mg, 0.28 mmol), and 3-bromo-4-methoxy-6-methyl-2-pyrone (123 mg, 0.56 mmol). ^{1}H NMR (δ): 6.66 (s, 1H, $=$CH), 5.33 (s, 5H, C_5H_5), 4.07 (s, 3H, OCH_3), 2.54 (s, 3H, CH_3). ^{13}C NMR (δ): 209.9 (s, M$-$$C$O), 170.6 (s), 169.8 (s), 164.9 (s), 98.9 (s, CH of 2-pyrone), 90.9 (s, CBr), 85.8 (s, C_5H_5), 58.7 (s, OCH$_3$), 19.1 (s, CH$_3$). MS FAB$^+$ (m/z): 395 M$^+$, correct isotopic distribution for $C_{14}H_{12}BrO_5Fe$; fragment ion peak at 339 (M $-$ 2 CO)$^+$. IR (CH_2Cl_2 solution, CsCl plates; cm^{-1}): 2070 (ν(CO)), 2025 (ν(CO)), 1663 (C$=$O), 1516 (pyrone backbone).

Attempts to gain satisfactory elemental analyses of the compounds were frustrated by contamination with trace quantities of free 2-pyrone and metallic residue in the crystallization process; however, the proposed elemental compositions are consistent with the observed isotope patterns in the mass spectra.

All of the procedures could also be performed on a larger scale (up to 1 mmol) with no significant effect on the course of the reaction.

Reaction of Complex 10 with PhC≡CPh. To a stirred dichloromethane (25 mL) solution of complex **10** (44 mg, 0.1 mmol) was added 42 mg (0.2 mmol) of PhC≡CPh. The subsequent reaction was monitored by IR spectroscopy. After a period of 95 h the color of the solution had changed from deep red to yellow and the bands due to the starting material in the metal$-$carbonyl region of the IR spectrum had vanished, to be replaced by a single peak at 2072 cm^{-1}, which was identical with that for an authentic sample of [Mo(CO)(η^2-PhC≡CPh)$_2$(η^5-C_5H_5)]$^+$.

X-ray Crystallography. Diffraction data were collected at 115 K on a Bruker Smart Apex diffractometer with Mo Kα radiation (λ = 0.710 73 Å) using a SMART CCD camera. Diffractometer control, data collection, and initial unit cell determination was performed using "SMART" (v5.625 Bruker-AXS). Frame integration and unit-cell refinement software was carried out with "SAINT+" (v6.22, Bruker AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined by full-matrix least squares using SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. Crystallographic data for the new complexes are given in Table 1.

Acknowledgment. We thank Professor Michael Green (University of Bristol) and Dr. Ciara O'Brien (National University of Ireland, Maynooth) for helpful discussions. J.M.L. and I.J.S.F. thank the University of York for startup funding.

Supporting Information Available: Tables giving full crystallographic data for **7**, **11**, **13**, and **14**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049523W