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Binuclear Iron(I), Ruthenium(I), and Osmium(I) Hexacarbonyl Complexes Containing a Bridging Benzene-1,2-dithiolate Ligand. Synthesis, X-ray Structures, Protonation Reactions, and EHMO Calculations[†]

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The dithiolate-bridged complexes $[M_2(\mu\text{-bdt})(CO)_6]$ (M = Fe (**1**), Ru (**2**), Os (**3**); bdt = benzene-1,2-dithiolate) have been prepared. X-ray diffraction studies have revealed that although the three compounds have analogous molecular structures their crystal structures are different as a result of different molecular packings. Complex **1** does not react with tetrafluoroboric acid in 1,2-dichloroethane, while compounds **2** and **3**, under the same conditions, undergo protonation at the metal atoms to give the cationic hydrido derivatives $[M_2(\mu\text{-H})(\mu\text{-bdt})(CO)_6][BF_4]$ (M = Ru, Os). EHMO calculations have been used to rationalize the results of the protonation reactions.

Introduction

It is well-known that a comparison of the inorganic chemistry of iron, ruthenium, and osmium results in more differences than analogies.[1] In the case of their organometallic chemistry, although many ruthenium and osmium compounds share common structures, their reactivity is in many cases quite different,[2] while both the structural and derivative chemistry of iron are generally quite unlike those of its heavier congeners.[2] For example, the synthetic routes leading to $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) are notably different,[3] as are also their reactivity patterns;[4] however, $[Ru_3(CO)_{12}]$[5] and $[Os_3(CO)_{12}]$[6] are isostructural, having all their CO ligands in terminal positions, while the structure of $[Fe_3(CO)_{12}]$ differs in that it contains two bridging CO ligands.[7] Another interesting example which reflects some of the analogies and also the differences between the three group 8 metals is comprised by the complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M = Fe, Ru, Os). Unlike the iron[8] and ruthenium[9] compounds, that present cis and trans isomers and contain two bridging CO ligands in the solid state at room temperature (they are fluxional in solution), the osmium dimer contains only terminal CO ligands.[10] The three compounds can be made by different synthetic methods.[11] It should be noted that although their electron count (34 electrons) and their diamagnetism suggest the existence of a metal−metal single bond, very little electron population has been found between the iron atoms by electron density measurements (X-ray and neutron diffraction methods at low temperatures)[8] and by theoretical calculations.[12,13]

We now report the synthesis of the dithiolate-bridged complexes $[M_2(\mu\text{-bdt})(CO)_6]$ (M = Fe, Ru, Os; bdt = benzene-1,2-dithiolate) and a comparative study of their molecular and crystal structures (X-ray diffraction), of their electronic structures (EHMO calculations), and also of some aspects of their reactivity. To our knowl-

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(11) Selected syntheses of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (M = Fe,[11a] Ru,[11b] Os[11c]) are described in: (a) King, R. B. In *Organometallic Syntheses*; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1965; Vol 1, p 114. (b) Doherty, N. M.; Knox, S. A. R.; Morris, M. J. *Inorg. Synth.* **1990**, *28*, 189. (c) Fischer, E. O.; Bittler, K. *Z. Naturforsch., B* **1962**, *17*, 274.

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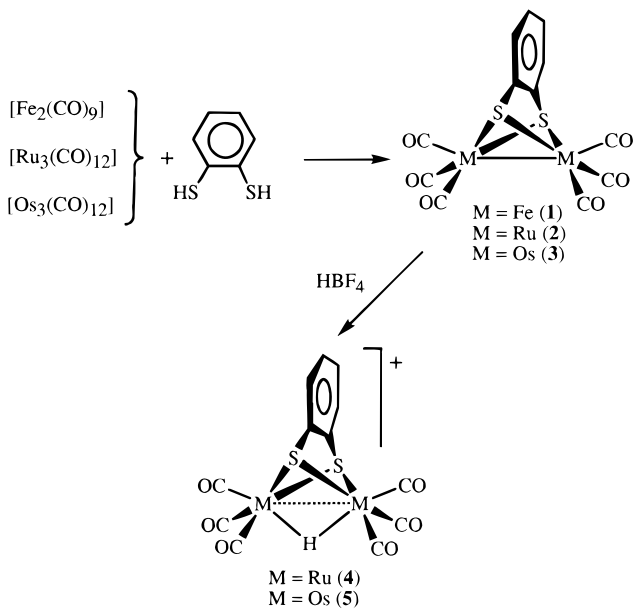
Scheme 1



edge, comparative studies of this kind on isostructural complexes of group 8 metals have not been carried out before. We chose these compounds because (a) it was anticipated that they would be preparable, since compounds having two bridging alkane- or arenethiolate ligands, such as $[M_2(\mu\text{-SR})_2(CO)_6]$ (M = Fe,[14] Ru[15]) or $[M_2(\mu\text{-edt})(CO)_6]$ (M = Fe,[16] Ru,[17] Os;[18] edt = ethane-1,2-dithiolate), were previously known, (b) the structures of these known bis(thiolate)-bridged complexes of the three metals (Fe, Ru, Os)[14−19] led us to expect that the benzenedithiolate derivatives would be isostructural, and (c) the benzenedithiolate bridge rules out the possibility of having syn and anti isomers which do exist in the bis(thiolate) complexes $[M_2(\mu\text{-SR})_2(CO)_6]$.[19]

Results and Discussion

Preparation of $[M_2(\mu\text{-bdt})(CO)_6]$ (M = Fe, Ru, Os). Treatment of $[Fe_2(CO)_9]$ with an excess of benzene-1,2-dithiol in THF at reflux (70 min) or room temperature (2 h), followed by a chromatographic workup, allowed the isolation of $[Fe_2(\mu\text{-bdt})(CO)_6]$ (**1**) in 45% yield (Scheme 1).

The ruthenium and osmium derivatives $[M_2(\mu\text{-bdt})(CO)_6]$ (M = Ru (**2**), Os (**3**)) were prepared in moderate (35% for **2**) to low (16% for **3**) yields by treating the corresponding trinuclear carbonyl $[M_3(CO)_{12}]$ with benzene-1,2-dithiol in toluene at reflux temperature. Both reactions gave mixtures of compounds from which **2** or **3** was separated by chromatographic methods. The use of solvents with boiling points lower than that of toluene resulted in lower yields of the desired compounds and/or longer reaction times. The three compounds gave satisfactory elemental analyses and correct molecular ion peaks in their FAB mass spectra. Their ^1H NMR spectra consist of two symmetric multiplets (AA′MM′ spin system), and their solution IR spectra in the carbonyl region have similar band patterns. All these data are in agreement with a common molecular structure for the three compounds.

Although relatively low, the yields obtained for **1**−**3** are comparable to those reported for other binuclear bis(thiolate)-bridged hexacarbonyl complexes of iron,[14,16,19] ruthenium,[15,17] and osmium.[18] The related ethane-1,2-dithiolate compounds $[M_2(\mu\text{-edt})(CO)_6]$ have been pepared in low yields by using 1,2,5,6-tetrathiacyclooctane (M = Fe,[16a] Ru[17a]), 1,4,7-trithiacyclononane (M = Ru),[17b] or 1,4-dithiacyclohexane (M = Os)[18] as precursors of the edt ligand. Direct reaction of ethanedithiol with $[Fe_3(CO)_{12}]$ gives $[Fe_2(\mu\text{-edt})(CO)_6]$ in high yield.[20] Over the past few years, several authors have reported general high-yield routes to diruthenium tetracarbonyl derivatives of the type $[Ru_2(\mu\text{-SR})_2(CO)_4(PR_3)_2]$,[21−23] but high-yield routes to the corresponding hexacarbonyls have yet to be discovered.

Solid-State Structural Studies. The molecular and crystal structures of **1**−**3** were determined by X-ray diffraction methods. At the molecular level, the three compounds are very similar, consisting of binuclear $M_2(CO)_6$ fragments in which each $M(CO)_3$ unit is attached to both sulfur atoms of a bdt ligand. The bridging ligand is planar and perpendicular to the M−M vector, resulting in an overall C_{2v} symmetry. As a representative example, Figure 1 shows the molecular structure of the ruthenium complex. For comparative purposes, a common atom-labeling scheme has been used for the three compounds. A selection of bond lengths and angles is given in Table 1. For homologous M−atom distances in the three complexes, the lengths involving iron are 0.10−0.17 Å shorter than those involving ruthenium or osmium, as a result of the smaller size of iron. The ruthenium and osmium compounds differ only very slightly in the distances between the heavier atoms (M or S) and the metals (0.01−0.03 Å in favor of osmium). Interesting features of the molecular structures of **1**−**3** are their very short M−M distances, 2.480(2), 2.650(2), and 2.686(2) Å, respectively, which to our knowledge are the shortest found for bis(thiolate)-bridged binuclear complexes of each metal.[24] For example, the M−M distances in the related compounds $[M_2(\mu\text{-edt})(CO)_6]$ are 2.497(4) Å for M = Fe[16a] and 2.710(1) Å for M = Os[18] (the corresponding ruthenium com-

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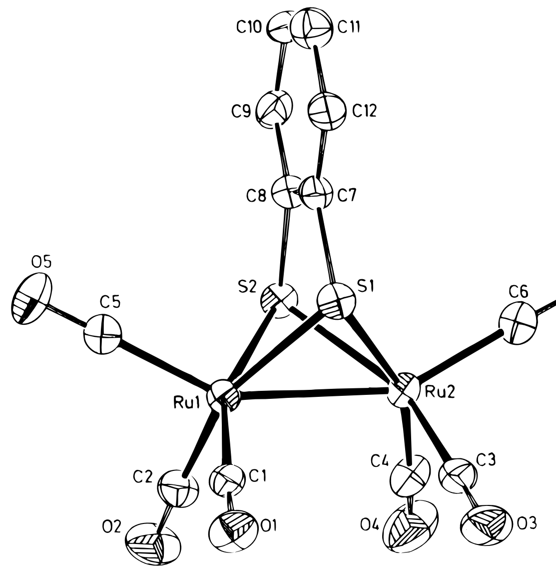

Figure 1. Molecular structure of $[Ru_2(\mu\text{-bdt})(CO)_6]$ (**2**).

Table 1. Selected Bond Lengths and Bond Angles in $[M_2(\mu\text{-bdt})(CO)_6]$

	M = Fe	M = Ru	M = Os
	Bond Lengths (Å)		
M(1)−M(2)	2.480(2)	2.650(2)	2.686(2)
M(1)−S(1)	2.271(2)	2.406(2)	2.428(6)
M(1)−S(2)	2.272(2)	2.406(6)	2.433(6)
M(2)−S(1)	2.262(2)	2.407(5)	2.425(6)
M(2)−S(2)	2.267(2)	2.412(2)	2.429(7)
M(1)−C(1)	1.779(7)	1.900(7)	1.99(4)
M(1)−C(2)	1.789(8)	1.905(9)	1.84(2)
M(1)−C(5)	1.807(8)	1.944(8)	1.99(3)
M(2)−C(3)	1.784(7)	1.886(6)	1.85(2)
M(2)−C(4)	1.795(7)	1.88(2)	1.94(4)
M(2)−C(6)	1.798(8)	1.955(6)	1.95(3)
C(1)−O(1)	1.137(7)	1.130(7)	1.07(4)
C(2)−O(2)	1.136(7)	1.12(1)	1.18(3)
C(3)−O(3)	1.130(7)	1.137(7)	1.12(4)
C(4)−O(4)	1.141(7)	1.13(2)	1.15(3)
C(5)−O(5)	1.127(7)	1.13(1)	1.07(3)
C(6)−O(6)	1.136(8)	1.116(7)	1.07(3)
	Bond Angles (deg)		
C(1)−M(1)−C(2)	93.2(3)	91.1(3)	89.5(12)
C(1)−M(1)−C(5)	99.7(3)	99.4(3)	98.0(13)
C(1)−M(1)−S(1)	88.8(2)	89.9(2)	93.5(9)
C(1)−M(1)−S(2)	158.9(2)	159.1(2)	159.1(12)
C(2)−M(1)−C(5)	100.0(3)	96.9(3)	95.7(10)
C(2)−M(1)−S(1)	156.5(2)	158.1(3)	159.2(9)
C(2)−M(1)−S(2)	89.4(2)	93.9(3)	92.9(9)
C(5)−M(1)−M(2)	149.2(2)	150.8(2)	152.0(7)
C(5)−M(1)−S(1)	102.7(2)	104.5(2)	104.3(7)
C(5)−M(1)−S(2)	100.4(2)	100.1(2)	102.3(7)
S(1)−M(1)−M(2)	56.68(5)	56.6(1)	56.3(2)
S(2)−M(1)−M(2)	56.80(5)	56.6(1)	56.4(2)
S(1)−M(1)−S(2)	80.66(6)	78.1(1)	77.2(2)

pound has not been characterized by diffraction methods). Prior to complex **2**, the shortest Ru−Ru distance in a bis(thiolate)-bridged binuclear complex of ruthenium was found in the bdt-bridged disubstituted complex $[Ru_2(\mu\text{-bdt})(CO)_4(PPh_3)_2]$ (2.6767(5) Å).[23] Therefore, it seems clear that the short M−M distances observed in the bdt-bridged complexes are imposed by the bdt ligand. Diruthenium(I) complexes containing the isoelectronic benzene-1,2-diamido or naphthalene-1,7-diamido ligands also have very short Ru−Ru distances.[25−27]

One would expect that compounds having closely related structures at the molecular level would exhibit similar crystal structures, but this is not the case for **1**−**3**. The three compounds crystallize in the monoclinic space group $P2_1/c$, but their cell parameters are quite different (Table 2) and a look at their unit cells (Figure 2) reveals different molecular packings for each complex. It should be noticed that the three compounds were crystallized under analogous conditions, that they do not cocrystallize with any solvent molecule, and that the corresponding X-ray diffraction data were taken at the same temperature. Although we are not aware of previous reports on observations of this type, a literature search on crystal data of compounds of different metals having common molecular structures has revealed that our observation with **1**−**3** is uncommon but not unique. For example, the iron complex $[Fe_2(\mu\text{-edt})(CO)_6]$ crystallizes in the triclinic space group $P\bar{1}$, with two independent molecules in the asymmetric unit ($Z = 4$),[16a] whereas the osmium complex $[Os_2(\mu\text{-edt})(CO)_6]$ crystallizes in the monoclinic space group $P2_1/n$.[18]

Table 2. Crystallographic and Refinement Data for $[M_2(\mu\text{-bdt})(CO)_6]$

	M = Fe	M = Ru	M = Os
formula	$C_{12}H_4Fe_2O_6S_2$	$C_{12}H_4O_6Ru_2S_2$	$C_{12}H_4O_6Os_2S_2$
fw	419.97	510.41	688.67
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	8.986(5)	11.67(2)	8.460(3)
b, Å	14.767(5)	11.142(5)	15.213(4)
c, Å	11.540(4)	12.95(3)	12.757(3)
β, deg	91.50(3)	104.8(2)	106.68(5)
V, Å^3	1531(1)	1628(4)	1572.8(8)
Z	4	4	4
F(000)	832	976	1232
D_{calcd}, g/cm^3	1.822	2.082	2.908
abs coeff, mm^{-1}	2.189	2.132	1.643
cryst size, mm	0.23 × 0.13 × 0.33	0.30 × 0.20 × 0.23	0.33 × 0.23 × 0.40
(h, k, l) ranges	(−10,0,0) to (13,17,13)	(0,0,0) to (13,13,14)	(−10,0,0) to (9,18,15)
θ range, deg	2.24−24.98	1.80−24.95	2.14−24.99
no. of measd rflns	3449	2678	3573
no. of unique rflns	2700	1335	2757
$R_{int} = \Sigma(I - \langle I\rangle)/\Sigma I$	0.055	0.029	0.077
no. of rflns with $I > 2\sigma(I)$	1410	1085	2036
no. of restraints, params	0, 200	0, 200	0, 200
$R(F)$ ($I > 2\sigma(I)$)^a	0.041	0.022	0.086
$R_w(F^2)$ (all data)^b	0.106	0.054	0.248
GOF^c	1.010	1.039	1.053
Δ/σ	0.001	0.001	0.002
max, min $\Delta\rho$, e/Å^3	0.49, −0.59	0.17, −0.24	2.83, −4.05

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] Goodness of fit (GOF) = $[\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

Protonation Reactions. The iron complex **1** remained unaltered when it was treated with an excess of tetrafluoroboric acid in dichloromethane or 1,2-dichloroethane solvent at room temperature. However, under analogous conditions, the ruthenium and osmium complexes **2** and **3** underwent protonation to give the cationic hydrido derivatives $[M_2(\mu\text{-H})(\mu\text{-bdt})(CO)_6][BF_4]$ (M = Ru (**4**), Os (**5**)). These compounds were precipitated as solids from the acidic solutions, but they underwent spontaneous deprotonation when they were

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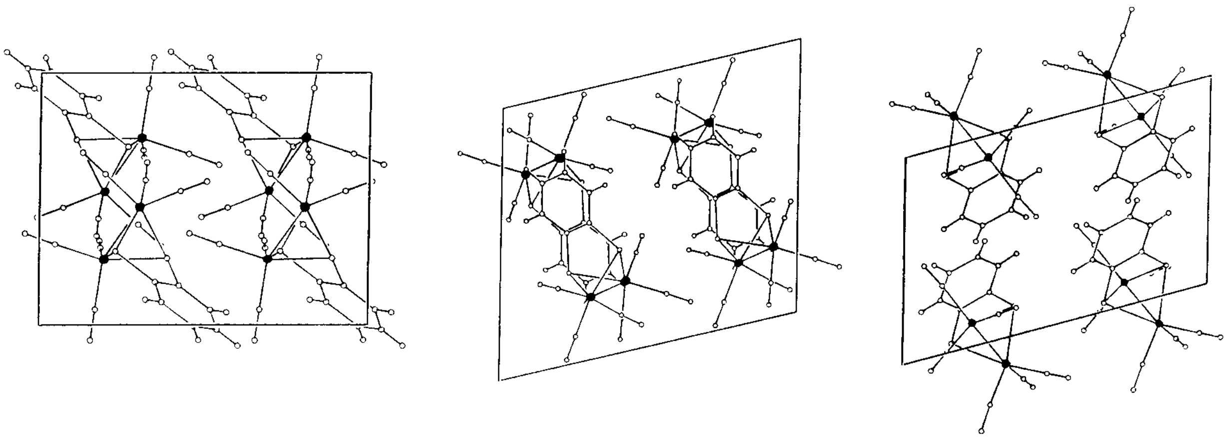

Figure 2. Unit cells of [M_2(*μ*-bdt)$(CO)_6$] (projections on the *ac* planes) for M = Fe (left), Ru (middle), and Os (right), showing the different packings of the molecules in the crystals of each compound.

dissolved in solvents which did not contain an excess of tetrafluoroboric acid.

The structures proposed for **4** and **5** in Scheme 1 are based on their analytical and spectroscopic data. Their IR spectra show the *ν*(CO) absorptions at higher wavenumbers than those of their parent compounds, confirming that protonation has reduced the electron density of the metals (this enhances the C−O bond order as a consequence of a decrease of electron donation by the metals to *π** CO orbitals). Their ^{1}H NMR spectra show the hydride ligand as a singlet, while the aromatic protons are observed as an AA′MM′ spin system, at chemical shifts different from those of the starting materials, confirming the C_{2v} symmetry of these protonated derivatives.

It has been reported that some other neutral binuclear ligand-bridged ruthenium(I) and osmium(I) complexes, such as [Ru_2(*μ*-dan)$(CO)_4(L)_2$] (H_2dan = 1,8-diaminonaphthalene; L = CO, PR_3)[26,27] and [Os_2(*μ*-$MeCO_2)_2(CO)_4(PR_3)_2$],[28] undergo protonation to give cationic hydride derivatives, but this reaction cannot be generalized to all ruthenium(I) and osmium(I) compounds of this kind,[25] since, for example, [Ru_2(*μ*-dmpz)$_2$-$(CO)_6$] (Hdmpz = 3,5-dimethylpyrazole) cannot be protonated in concentrated sulfuric acid.[29] To our knowledge, no metal-protonation reactions of neutral binuclear ligand-bridged iron(I) complexes have been reported.

As the different reactivity found for **1**, as compared to that of **2** and **3**, has to be due to electronic factors, theoretical calculations were carried out in order to get information that could help rationalize the experimental results.

EHMO Calculations. To allow comparisons of numerical EHMO calculation results obtained for complexes of different metals, it is essential to use a homogeneous set of EH parameters.[30] The set of parameters used in this work for iron, ruthenium, and osmium has been recently computed from isostructural carbonyl complexes with the metals in a formal oxidation state of 0.[30] On the other hand, the determination of the molecular structures of compounds **1**−**3** by X-ray diffraction methods provided us with adequate structural data to be used in the calculations.

Table 3. Selected Results of EHMO Calculations on [M_2(*μ*-bdt)$(CO)_6$]

	M = Fe	M = Ru	M = Os
M−M overlap population, e	0.079	0.120	0.194
M−S overlap population, e	0.619	0.507	0.609
net charge on each M	+0.547	+0.325	+0.119
net charge on each S	−0.585	−0.660	−0.556
LUMO composition, %	14.8 Fe, 74.0 bdt, 11.2 CO	23.2 Ru, 64.2 bdt, 12.6 CO	19.4 Os, 69.8 bdt, 10.8 CO
HOMO composition, %	43.6 Fe, 43.2 bdt, 13.2 CO	61.4 Ru, 4.9 bdt, 33.7 CO	64.0 Os, 9.6 bdt, 26.4 CO
LUMO energy, eV	−10.165	−10.389	−10.284
HOMO energy, eV	−11.738	−11.582	−11.753

The calculations revealed that the M−M overlap population (OP) values for the three complexes decrease in the order **3** > **2** > **1** (Table 3) and it is generally accepted that the smaller the M−M OP value, the weaker the M−M interaction associated with it.[31] However, as the M−M bond distances of **1**−**3** are very short and decrease in the order **3** > **2** > **1**, it can be concluded that the “pincer” effect of the bridging bdt ligand has a stronger influence on the M−M distance than the strength of the M−M interaction.

Table 3 shows that the net charges in the metal atoms decrease on going from **1** to **2** and **3**. These data, which indicate that the metal atoms of **1** are poorer in electron density than those of **2** or **3**, are in agreement with the experimental results obtained upon treatment of **1**−**3** with protic acids (**1** did not undergo protonation, whereas **2** and **3** did). Morever, a look at the frontier molecular orbitals of **1**−**3** (Figure 3) indicates that the HOMO of the iron compound **1** is very different from those of **2** and **3**. While the HOMO of **1** has b_1 symmetry and has a large contribution of orbitals of the bdt ligand, the HOMOs of **2** and **3** are of a_1 symmetry and have a much higher metallic character. As the 1s orbital of the proton is of a_1 symmetry, its interaction with the HOMO of **1** is nonbonding (symmetry forbidden), while its interaction with the HOMOs of **2** and **3** is of bonding character (symmetry allowed). In fact, an analysis of the interaction of the proton with complex **2** to give **4**

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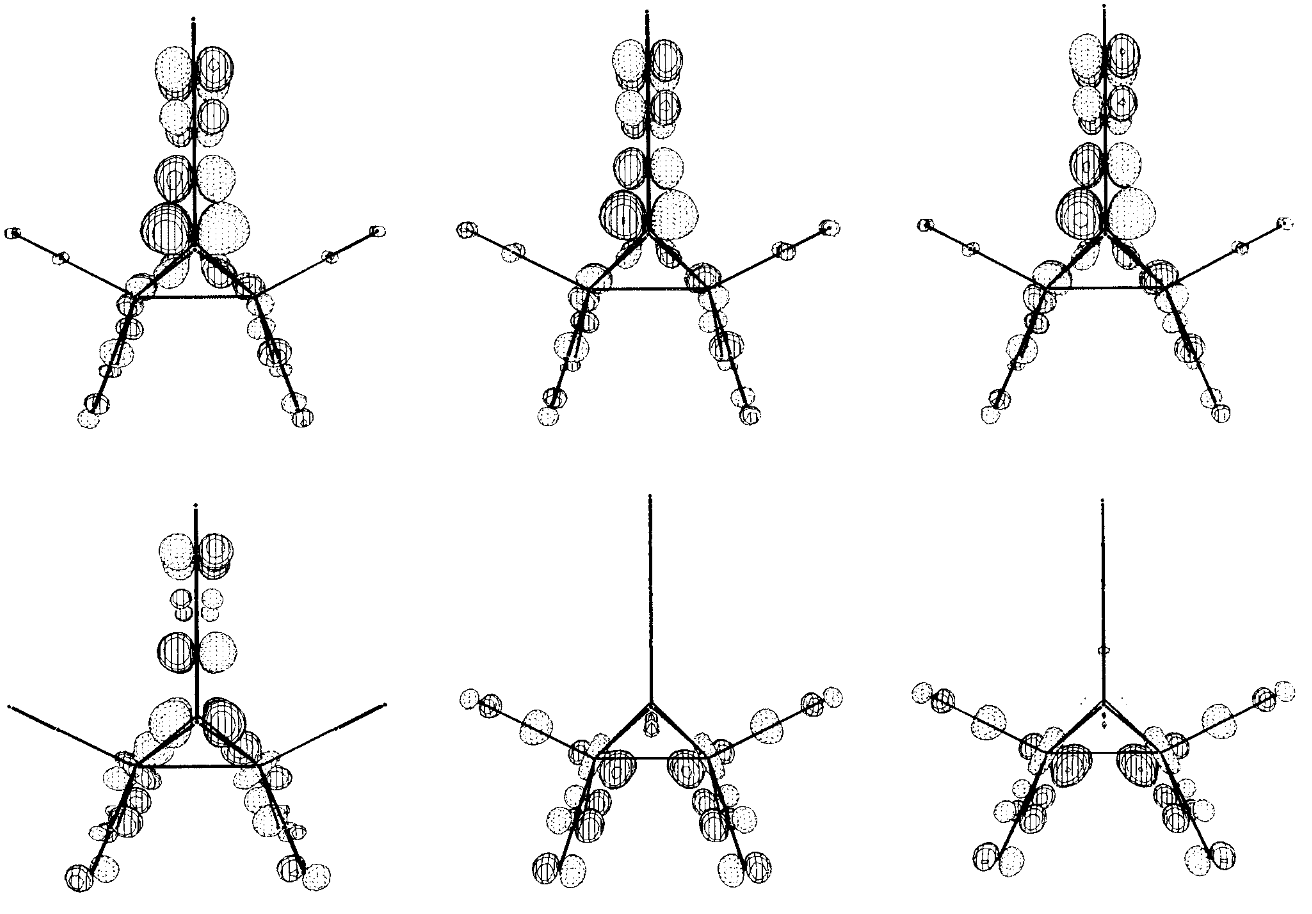

Figure 3. CACAO plots of the LUMOs (top) and HOMOs (bottom) of [$M_2(\mu\text{-bdt})(CO)_6$] for M = Fe (left), Ru (middle), and Os (right).

revealed that the HOMO of **2** is indeed the FMO that most overlaps with the proton 1s orbital (with an overlap integral of 0.53, while other MOs of **2** of a_1 symmetry give overlap integrals ≤ 0.02). In addition, the highest occupied MO of a_1 symmetry of compound **1** (orbital $21a_1$) has a 56.4% contibution of the bdt ligand and only a 43.3% contribution of the iron atoms, disfavoring protonation at the metal atoms (the metal contributions to the HOMOs of **2** and **3** are 61.4% and 64.4%, respectively). Therefore, the protonation reactions of compounds **1**−**3** are orbital- as well as charge-controlled reactions.

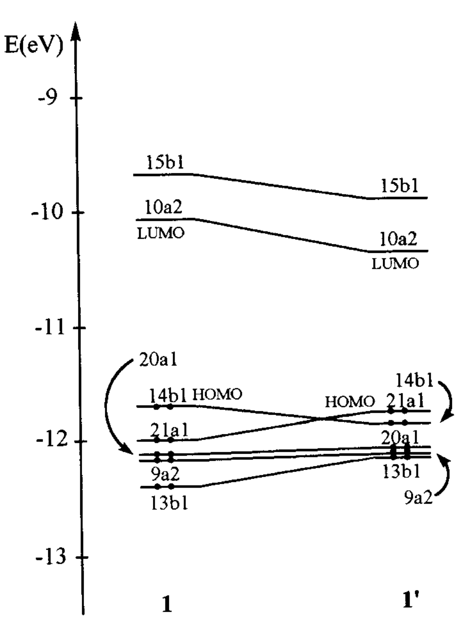

Figure 4. Selected MO energy changes occurring on transforming the iron compound **1** into the fictitious compound **1′** (which has structural parameters identical with those of the ruthenium compound **2**).

These EHMO results rationalize the protonation reactions of **1**−**3**, but they raise another question: why are the MOs of the iron compound so different from those of **2** and **3**? To see whether the answer is related to the different structural parameters of these complexes (as noted above, the M−atom bond lengths in **1** are 0.2−0.1 Å shorter than the corresponding distances in **2** and **3**; see Table 1), we carried out a calculation on a fictitious iron compound **1′**, structurally identical with the ruthenium complex **2** (same bond distances and angles as in **2**, but with iron in place of ruthenium). In this case the results of the calculation were similar to those obtained with complex **2** (Figure 4). For example, the orbital $21a_1$, which in **1** has a 56.4% contribution of the bdt ligand, is transformed into the HOMO of **1′**, which only has 8.9% of bdt ligand orbitals. Another significant change is observed for the orbital $14b_1$ (the HOMO of **1**), which decreases its energy by 0.18 eV when **1** is converted into **1′**. The net charge of the metal atoms in **1′** is +0.261. Thus, small modifications in structural parameters result in significant changes in MO composition that are accompanied by important variations of the MO energies and the atom charges. In conclusion, the smaller size of the iron atom, as compared to those of ruthenium and osmium, is responsible for the differences observed between compound **1** and compounds **2** and **3**.

These results clearly indicate that, to carry out theoretical calculations, it is very important to use real structural parameters. Therefore, results obtained from calculations on "model" compounds, for which no experimental structural data are available, should be interpreted with caution.

Experimental Section

General Synthetic and Analytical Data. Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk tubes and vacuum line techniques, and were routinely monitored by solution IR spectroscopy (CO stretching region) and by spot TLC on silica gel. Chromatographic separations were carried out in air. The compounds $[M_3(CO)_{12}]$ (M = Ru, Os) were purchased from Strem Chemicals; all other reagents were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. ^1H NMR spectra were run at room temperature with a Bruker AC-300 instrument, using internal $SiMe_4$ as standard (δ 0). Fast atom bombardment (FAB) mass spectra were obtained on a Finningan Mat-95 spectrometer, using nitrobenzyl alcohol as matrix and cesium as bombarding gas. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Fe_2(\mu\text{-bdt})(CO)_6]$ (1). A mixture of $[Fe_2(CO)_9]$ (100 mg, 0.275 mmol) and benzene-1,2-dithiol (35 μL, 0.302 mmol) was stirred in THF (10 mL) at reflux temperature for 70 min to give a blood red solution containing some black solid in suspension. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was redissolved in hexane (2 mL) and the solution was applied to a column of neutral alumina (activity I, 10 × 2 cm) packed in hexane. Hexane eluted a dark orange band which afforded compound **1** as a red-orange solid (52 mg, 45%). Anal. Found: C, 34.27; H, 1.02. Calcd for $C_{12}H_4Fe_2O_6S_2$: C, 34.32; H, 0.96. MS (*m/z*): 420 (M^+). IR ν(CO) (hexane): 2079 (m), 2044 (s), 2006 (vs), 1967 (vw), 1958 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): 7.13 (m), 6.63 (m) ppm.

$[Ru_2(\mu\text{-bdt})(CO)_6]$ (2). A solution of $[Ru_3(CO)_{12}]$ (200 mg, 0.313 mmol) and benzene-1,2-dithiol (54 μL, 0.649 mmol) in toluene (10 mL) was stirred at reflux temperature, under an atmosphere of carbon monoxide, for 35 min. The color changed from orange to orange-red, and some red-orange solid precipitated. The filtered solution was concentrated to ca. 2 mL and was applied to a column of neutral alumina (activity I, 10 × 2 cm) packed in hexane. Hexane eluted a pale yellow band which gave compound **2** as a yellow solid (83 mg, 35%). Anal. Found: C, 28.38; H, 0.74. Calcd for $C_{12}H_4O_6Ru_2S_2$: C, 28.24; H, 0.79. MS (*m/z*): 510 (M^+). IR ν(CO) (hexane): 2089 (m), 2062 (vs), 2016 (vs), 2012 (vs), 1977 (vw), 1967 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): 7.24 (m), 6.70 (m) ppm.

$[Os_2(\mu\text{-bdt})(CO)_6]$ (3). A mixture of $[Os_3(CO)_{12}]$ (100 mg, 0.110 mmol) and benzene-1,2-dithiol (22 μL, 0.187 mmol) was stirred in toluene (10 mL) at reflux temperature for 3 h. The color changed from pale yellow to brown-yellow. Some dark green solid precipitated. The filtered solution was concentrated to ca. 2 mL and was applied to preparative TLC plates (silica gel). Hexane−dichloromethane (5:3) eluted two bands. The second band (orange) contained a mixture of hydride compounds (^1H NMR), which was not investigated further. The first and fastest moving band (yellow) afforded compound **3** as a very pale yellow solid (12 mg, 16%). Anal. Found: C, 21.05; H, 0.65. Calcd for $C_{12}H_4O_6Os_2S_2$: C, 20.93; H, 0.58. MS (*m/z*): 688 (M^+). IR ν(CO) (hexane): 2089 (m), 2059 (s), 2002 (vs), 1990 (m), 1959 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.40 (m), 6.69 (m) ppm.

$[Ru_2(\mu\text{-H})(\mu\text{-bdt})(CO)_6][BF_4]$ (4). An excess of $HBF_4{\cdot}OEt_2$ (two drops from a pasteur pipet) was added to a solution of compound **2** (50 mg, 0.098 mmol) in 1,2-dichloroethane (5 mL). The reaction was instantaneous, as indicated by a color change from yellow to very pale yellow and by a drastic change in the IR spectrum of the solution. The solvent was removed under vacuum, and the residue was washed with diethyl ether (3 × 5 mL) to give complex **4** as a pale yellow solid (50 mg, 85%). The compound spontaneously deprotonates when dissolved in acid-free solvents. Anal. Found: C, 23.89; H, 0.95. Calcd for $C_{12}H_5BF_4O_6Ru_2S_2$: C, 24.09; H, 0.84. MS (*m/z*): 511 (M^+). IR ν(CO) (1,2-dichloroethane + $HBF_4{\cdot}OEt_2$): 2148 (m), 2132 (vs), 2087 (vs) cm^{-1}. ^1H NMR ($CDCl_3$ + $HBF_4{\cdot}OEt_2$): 7.51 (m), 7.00 (m), −11.46 (s, μ-H) ppm.

$[Os_2(\mu\text{-H})(\mu\text{-bdt})(CO)_6][BF_4]$ (5). This complex was prepared as described above for compound **4**, from **3** (50 mg, 0.073 mmol) and $HBF_4{\cdot}OEt_2$. White solid (45 mg, 80%). It spontaneously deprotonates when dissolved in acid-free solvents. Anal. Found: C, 18.38; H, 0.73. Calcd for $C_{12}H_5BF_4O_6Os_2S_2$: C, 18.56; H, 0.65. MS (*m/z*): 689 (M^+). IR ν(CO) (1,2-dichloroethane + $HBF_4{\cdot}OEt_2$): 2144 (w), 2127 (vs), 2070 (vs) cm^{-1}. ^1H NMR ($CDCl_3$ + $HBF_4{\cdot}OEt_2$): 7.60 (m), 7.01 (m), −11.80 (s, μ-H) ppm.

X-ray Diffraction Studies. Dark red (**1**), yellow (**2**), and pale yellow (**3**) crystals, obtained by keeping a pentane solution of the corresponding complex at −20 °C for several weeks, were used for the X-ray diffraction studies. Intensities were measured at room temperature on an Enraf-Nonius CAD4 diffractometer, using Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\ 73$ Å) and the $\omega{-}2\theta$ scan method. A selection of crystal and refinement data for the three compounds is given in Table 3.

The cell dimensions were determined by least-squares refinement of 25 high-order reflections with $13 \leq \theta \leq 16°$ (**1**), $15 \leq \theta \leq 20°$ (**2**), and $15 \leq \theta \leq 18°$ (**3**). Systematic absences determined the space group as $P2_1/c$ for the three compounds. Intensities were collected with a scan angle of 1.5° and a variable scan rate with a maximun scan time of 60 s per reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.99 and 1.04 (**1** and **2**) and 0.98 and 1.03 (**3**). Profile analysis was performed on all reflections.[32] Lorentz and polarization corrections were applied.

The structures were solved by the Patterson method using DIRDIF92.[33] Isotropic least-squares refinements, using a local version[34] of SHELX,[35] were followed by an empirical absorption correction, using XABS2.[36] The maximum and minimum correction factors were respectively 1.00 and 0.43 (**1**), 1.00 and 0.70 (**2**), and 1.00 and 0.24 (**3**). Full-matrix anisotropic least-squares refinements on F^2, using SHELXL92,[37] of all the non-hydrogen atoms, followed by Fourier synthesis maps, allowed the location of all hydrogen atoms. Hydrogen atoms were

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refined isotropically with a common thermal parameter, constraining the bond angles but with free distances to their parent atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$: $w = 1/[\sigma^2(F_o^2) + (nP)^2]$ ($n = 0.0396$ (**1**), 0.0301 (**2**), 0.1772 (**3**)), with $\sigma(F_o^2)$ from counting statistics and $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. Atomic scattering factors were taken from the literature.[38] Geometrical calculations were made with PARST.[39] The structure plots were drawn with the EUCLID package.[40] All calculations were carried out on an Alpha AXP-3000 workstation at the Scientific Computer Center of the University of Oviedo.

EHMO Calculations. Theoretical MO calculations were carried out at the extended Hückel level,[41] using the CACAO program.[42] The geometrical parameters used for **1**−**3** were based on their X-ray diffraction data, averaging the appropriate distances and angles in order to obtain ideal C_{2v} symmetry. The geometrical parameters used for compound **4** were based on those obtained experimentally for the structurally related compound $[\mathrm{Ru_2}(\mu\text{-AgPPh}_3)(\mu\text{-dan})(\mathrm{CO})_4(\mathrm{PPr^i}_3)_2][\mathrm{BF_4}]$.[28] The orbital parameters used in the calculations (see the Supporting Information) were those implemented in CACAO,[42] except those of the sulfur 3d orbitals[43] and those of the iron, ruthenium, and osmium atomic orbitals,[30] which were taken from the literature. We performed sets of calculations including and excluding the sulfur 3d orbitals, but the latter gave somewhat unrealistic conclusions since they resulted in no electron retrodonation at all from the metal atoms to the bdt ligand. Therefore, although there is a controversy about the role played in the bonding by the d orbitals of main-group elements,[30] we felt inclined to the inclusion of the sulfur 3d orbitals in the calculations.

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for **1**−**3** (19 pages). Ordering information is given on any current masthead page.

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