Table I. Effects of ^{18}O on ^{31}P NMR Chemical Shifts of AMPS and *S*-Methyl-AMPS

^{18}O species	δ_P[a]	$\Delta\delta_P$[b]
AMPS	43.200	
[α-^{18}O]AMPS	43.167	0.033
[α-$^{18}O_2$]AMPS	43.134	0.033
S-methyl-AMPS	22.642	
S-methyl-[α-^{18}O]AMPS	22.607	0.035
S-methyl-[α-$^{18}O_2$]AMPS	22.572	0.035

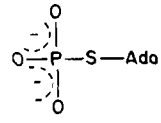
[a] ^{31}P NMR chemical shift relative to an external standard of 85% H_3PO_4, in ppm. Spectra recorded at pH 8.5. [b] $\Delta\delta_P$ is defined as the absolute difference beteen δ_P for the ^{18}O-containing species relative to ^{16}O species and divided by the number of chemically equivalent ^{18}O's in the species, in ppm.

I are consistent with bond orders of 1.5 since the $\Delta\delta_p$ value for single-bonded ^{18}O in phosphorothioates is 0.022.[6a,b]

If **1a** accurately represented the P–O bonding in AMPS, methylation to **2** would increase the P–O bond order from 1 to 1.5; and this would be reflected in a proportional increase in the ^{18}O-isotope shift. As shown in Table I, this transformation is accompanied by only a slight increase in the ^{18}O-isotope shift.

The small difference between $\Delta\delta_p$ for [^{18}O]AMPS and *S*-methyl-[^{18}O]AMPS may be within experimental error. If significant, it could reflect slightly higher P–O bond order in *S*-methyl-AMPS compared with AMPS. In this case, taking 1.5 as the P–O bond order in *S*-methyl-AMPS (**2**), the P–O bond order in AMPS could be as small as 1.4, which would not alter our conclusion that **1b** is a reasonably accurate representation of bonding in AMPS, whereas **1a** is not.

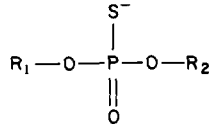
Ash et al.[7] have suggested that differences in ^{31}P NMR chemical shifts such as those for AMPS and *S*-methyl-AMPS in Table I reflect differences in P–S bond orders, that for *S*-methyl-AMPS being 1.0. These differences should not be attributed solely to bond order, however, since the ^{31}P NMR chemical shift for *S*-5′-adenosyl phosphorothioate, **3**, is 12.4 ppm[8] compared with 22.6



3

ppm for **2**, despite the fact that sulfur is bridging with a P–S single bond in both compounds. Differences in ^{31}P chemical shifts among phosphorothioates are poorly understood, but appear not to be determined by bond order alone and may be dominated by other factors.

The structure **1b** for AMPS suggests structure **4** for nucleoside



4

R_1 = 5′-nucleoside; R_2 = H, 3′-nucleoside, PO_3^{2-}, $P_2O_7^{3-}$

phosphorothioates in general. This formulation is consistent with the differences in ^{18}O-isotope shift effects on the ^{31}P NMR resonances of nucleoside phosphorothioates such as ADPαS and ATPβS with bridging and nonbridging ^{18}O.[6a,b,9] It is also consistent with the vibrational spectra of thiophosphate trianion and dianion in aqueous solutions[10a,b] as well as with the relative acid strengths of phosphoric and thiophosphoric acids.[11]

Structural formulation **4** should guide rationalizations of nucleoside phosphorothioate interactions with enzymes. For example, S_P 3′,5′-cyclic AMPS activates 3′,5′-cyclic AMP dependent protein kinase, whereas the R_P epimer binds but does not activate.[12a,b] Since the configuration at phosphorus governs the regulatory properties of these compounds, it is very likely that an intimate interaction of the phosphorothioate center with the regulatory protein is involved in activation. Charge localization and bond orders at this center might be crucial factors in determining regulatory function. Secondary structure in sulfur analogues of oligonucleotides and polynucleotides may also be influenced by configuration and charge distribution at phosphorothioate diester centers.

It is emphasized that structure **4** refers to species not complexed with metal ions. The charge distribution in Mg^{2+} or Cd^{2+} complexes can vary, shifting from O in the presence of the former to S in the presence of the latter,[12-14] depeneding on the hardness or softness of the metal.

Acknowledgment. We are grateful to Professor T. Farrar and Christine A. Roeske of the Department of Chemistry and E. Mooberry of the Department of Biochemistry, University of Wisconsin, for assistance with the collection of NMR data. This work was supported by Grant GM30480 from the National Institute of General Medical Sciences.

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Hydride-Rich Zirconium–Osmium and Zirconium–Rhenium Dimers

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Heterobimetallic compounds offer the advantage of cooperativity between two adjacent, yet electronically different, metal centers and hold promise in the reduction of dipolar substrates such as CO or CO_2.[1,2] While many such dimeric species are known,[1-9] few have exhibited catalytic behavior in reactions of

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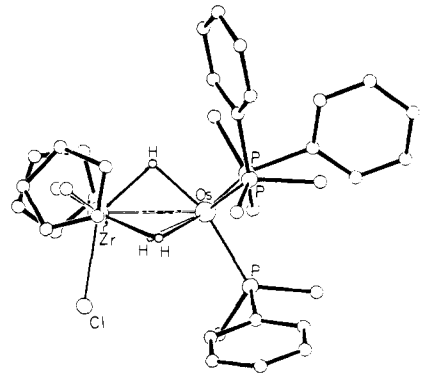

Figure 1. ORTEP drawing of one molecule of $Cp_2ClZrH_3Os(PMe_2Ph)_3$. Presumed hydride bridge locations have been added, trans to Os–P bonds, using M–(μ_2-H) distances from $[(C_5H_4Me)_2ZrH_2]_2$[21] and $H_2Os_3(CO)_{10}$.[22] Unlabeled atoms represent carbon. Selected structural parameters: Os–Zr 2.805 (1), Os–P 2.300 (3)–2.330 (3), Zr–Cl 2.521 (3) Å; ∠Zr–Os–P 117.7 (1)–123.4 (1)°, ∠P–Os–P 94.1 (1)–100.8 (1)°, ∠Cl–Zr–Os 98.6(1)–98.9 (1)°.

this type.[1] The difficulty has been the inroduction of hydride ligands to the preformed dimers, which often show no reaction with H_2.[10] We report here a different approach, a systematic synthesis of dimers from monomeric hydride-containing precursors, to yield heterobimetallic compounds rich in reducing (hydride) ligands.

Reaction of KH with $OsH_4(PMe_2Ph)_3$[11] or $ReH_7(PMePh_2)_2$[12] proceeds, with evolution of H_2, to give [K][*fac*-$OsH_3(PMe_2Ph)_3$] (**1**)[13] and [K][$ReH_6(PMePh_2)_2$] (**2**).[14] The anion in **1** has been generated and used in situ (after filtration of excess KH), whereas **2** is readily precipitated and isolated after filtration and addition of toluene. Both yellow anions revert to their neutral precursors in the presence of traces of water.

When salts **1** or **2** are mixed with equimolar $Cp_2Zr(X)Cl$, the reactions in eq 1 and 2 proceed with the formation of the first

$$[K][OsH_3(PMe_2Ph)_3] + Cp_2Zr(X)Cl \xrightarrow[THF]{} Cp_2Zr(X)[OsH_3(PMe_2Ph)_3] + KCl \quad (1)$$

3a, X = Cl
3b, X = H

$$[K][ReH_6(PMePh_2)_2] + Cp_2Zr(X)Cl \xrightarrow[THF]{} Cp_2Zr(X)[ReH_6(PMePh_2)_2] + KCl \quad (2)$$

4a, X = O-*i*-Pr
4b, X = H
4c, H = CH_3

known Zr/Os and Zr/Re mixed-metal dimers.[15,16] Compound **4c** is also formed from Cp_2ZrMe_2 and $ReH_7(PMePh_2)_2$ in toluene at 45 °C, but other products are also evident (^{31}P NMR).

For compounds **3a,b** NMR spectra (both ^1H and ^{31}P) show signals arising from an AA′A″XX′X″ system (similar to anion **1**). All rhenium-bound hydrides in **4a–c** appear equivalent at 25 °C and 360 MHz; no change is seen in **4a** at −85 °C. The NMR data also indicate that the zirconium-bound hydrides in **3b** and **4b** fail to exchange (on the NMR time scale) with Os–H or Re–H; resolution of a 1-Hz coupling between Zr–H and Re–H in **4b** rules out any dissociative equilibrium involving this dimer.

The nature of the linkage between the Cp_2ZrCl and H_3OsP_3 ($P{\equiv}PMe_2Ph$) fragments in **3a** was established by X-ray diffraction[17] (Figure 1). The hydride positions, known to be trans to the three Os–P vectors because of the AA′A″XX′X″ ^1H and ^{31}P NMR patterns, all occupy bridging sites. The possibility that one or more of the hydrides is terminal on Os is also excluded since the six[17b] Os–P distance are identical; bridging and terminal hydrides exhibit very different trans effects (~0.1 Å). Moreover, all six Zr–Os–P angles are identical and compare well to the 123° Os–Os–P angle in face-shared octahedral $P_3Os(\mu\text{-}H)_3OsP_3^+$.[18a] The chloride is terminal on zirconium (Cl···Os = 4.04 Å). The η^3 attachment of *fac*-$H_3OsP_3^-$ to zirconium[18b] contrasts to $Cp_2ZrH(\eta^2\text{-}BH_4)$,[19] and results in diminished Cl → Zr π donation (Zr–Cl = 2.521(4) Å in **3a**, compared to 2.441 (5) Å in Cp_2ZrCl_2).[20] The Cp centroid–Zr–Cp centroid angle of 121.4°, the smallest yet observed, illustrates the large steric demand of the $H_3Os(PMe_2Ph)_3$ unit. The Zr–Os distance, 2.805 (1) Å, is shorter than the length of the unbridged Zr–Ru bond (2.910 (1) Å) in $Cp_2Zr(O\text{-}t\text{-}Bu)[Ru(CO)_2Cp]$.[3c] The rotational conformation about the Zr–Os line in **3a** is sterically reasonable in that Cl lies between two bridging hydrides. Nevertheless, the NMR equivalence of the hydride ligands, of the phosphorus nuclei, and of

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(13) K[$OsH_3(PMe_2Ph)_3$]: 40.5-MHz $^{31}P\{^1H\}$ NMR (THF) −30.1 ppm (s), this becomes the symmetric multiplet of an AA′A″XX′X″ spin system on selective coupling to the hydride hydrogen; 220-MHz ^1H NMR (16 °C) 7.89 and 7.20 (PPh, m), 1.54 (PMe, d, J = 7 Hz), −11.6 ppm (OsH, AA′A″XX′X″, m).

(14) [K][$ReH_6(PMePh_2)_2$]: 40.5-MHz $^{31}P\{^1H\}$ NMR (THF) 11.40 ppm (s); 360-MHz ^1H NMR (THF-d_8) 7.59, 7.03 ppm (PPh, m), 1.86 (PMe, d, J = 7 Hz), −7.96 ppm (ReH, t, J = 15 Hz); IR (Nujol) 1938 (w), 1872 (m), 1842 (s) cm^{-1}.

(15) (a) **3a**: $^{31}P\{^1H\}$ NMR (C_6D_6) −27.85 ppm (s); ^1H NMR (C_6D_6): 7.70, 7.30 (PPh, m), 6.14 (Cp, s), 1.56 (PMe, d, J = 6 Hz), −7.05 ppm (OsH, *m*); IR (Nujol) 1952 (m), 1680 (br m) cm^{-1}. (b) **3b**: $^{31}P\{^1H\}$ NMR (THF) −24.50 (s); ^1H NMR (C_6D_6) 7.60, 7.2 (PPh, m), 5.96 (Cp, s), 4.74 (ZrH, br s), 1.53 (PMe, d, J = 6 Hz), −8.47 ppm (OsH, m); IR (Nujol) 1970 (br m), 1860 (br m), 1680 (br m) cm^{-1}.

(16) (a) **4a**: $^{31}P\{^1H\}$ NMR (THF) 8.90 ppm (s); ^1H NMR (C_6D_6) 6.8–7.8 (PPh, m), 6.14 (Cp s), 4.05 (C*H*Me$_2$, sept, J = 4 Hz), 1.98 (PMe, d, J = 7 Hz), 1.0. (CH*Me*$_2$, d J = 4 Hz), −5.10 ppm (ReH, t, J = 12 Hz). (b) **4b**: $^{31}P\{^1H\}$ NMr (hexane) 10.90 (s); ^1H NMR (C_6D_6) δ 7.56, 7.02 (PPh, m), 5.97 (Cp, s), 3.57 (ZrH, m), 1.89 (PMe, d, J = 8 Hz), −4.83 ppm (ReH, t (J = 14 Hz) of d (J = 1 Hz)); IR (THF) 1905 (m), 1815 (w), 1710 (br w), 1565 (br m) cm^{-1}. The 1.89 and −4.83 resonances integrate 1:1. (c) **4c**: $^{31}P\{^1H\}$ NMR (THF) 9.07 ppm (s); ^1H NMR (C_6D_6) δ 7.5, 6.9 (PPh, m), 5.91 (Cp, s), 1.89 PMe, d, J = 7 Hz), 0.17 (ZrMe, s), −4.81 ppm (ReH, t, J = 14 Hz). The 1.89 and −4.81 ppm resonances integrate 1:1.

(17) (a) Crystallographic data (−162 °C) for crystals grown from THF/toluene/hexane: a = 15.111 (4) Å, b = 26.541 (7) Å, c = 10.931 (2) Å, V = 4132.5 Å^3, Z = 4 in space group $P\bar{1}$; R_F = 5.2%. Disorder in toluene and *n*-hexane solvent in the lattice prevented location of hydride positions. (b) There are two crystallographically independent (but nearly identical) metal complexes in the unit cell; average values are quoted here.

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the methyl groups establishes facile rotation about the Zr–Os line (the process maintains the integrity of each trans H–Os–P vector).

The presence of low-energy stretching frequencies (e.g., 1710 and 1565 cm^{-1} in **4b**) suggests hydride bridges are also present in compounds **4**.

The wide variety of M–H, M′–H, and M–H–M′ bonds present in **3** and **4**, as well as the potential for creating unsaturation by H_2 or CH_4 elimination from **3b**, **4b**, and **4c**, motivate our current reactivity studies.

Acknowledgment. We thank NSF (CHE-8305281) for financial support, and Johnson, Matthey Co. for the loan of chemicals. We thank Scott Horn for skilled technical assistance.

Supplementary Material Available: Listing of atom coordinates, bond lengths, and bond angles for $Cp_2ZrClH_3Os(PMe_2Ph)_3$ (6 pages). Ordering information is given on any current masthead page.

Iron(III)-Catalyzed Oxygenation of Catechols. Structure of (Nitrilotriacetato)(3,5-di-*tert*-butylcatecholato)-ferrate(III) Dianion

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A variety of metal complexes have been reported that effect the oxidative cleavage of catechols.[1-7] These systems serve as models for the reactions catalyzed by catechol 1,2-dioxygenase and protocatechuate 3,4-dioxygenase, enzymes in which the proposed mechanism of oxygen incorporation involves substrate activation by the active site ferric center.[8] One system of particular interest is that reported by Weller and Weser,[7] consisting of the Fe(III)–nitrilotriacetate complex in an organic solvent–borate buffer mixture, the only Fe(III) system thus far that shows catechol cleavage activity. Over a period of days and in the presence of oxygen, 3,5-di-*tert*-butylcatechol is catalytically converted to 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-furanone in 80% yield, the highest reported for any model system to date.

Under the appropriate conditions, salts of $[Fe(NTA)DBC]^{2-}$[9] can be isolated with a stoichiometry that suggests that the catecholate ligand is chelated to the iron. This complex reacts with oxygen in DMF over 4 days to yield cleavage product in 80% yield. The reactivity of this complex contrasts that of a related system, $[Fe(salen)DBC]^-$, which is reported to be unreactive toward dioxygen.[10] The lack of reactivity of $[Fe(salen)DBC]^-$ has been suggested to arise from the stability of the chelated structure. The $E^{\circ\prime}$ for the DBSQ/DBC couple was found to be -423 mV vs. SCE in the complex as compared to -1340 mV in the free ligand,[11] a stabilization of the catecholate oxidation state by nearly a volt. Electrochemical studies of $[Fe(NTA)DBC]^{2-}$ show even greater stabilization for the DBSQ/DBC couple in this complex; $E^{\circ\prime}$ is found to be -268 mV vs. SCE in DMF. Thus electron transfer from both chelated catecholate complexes to dioxygen is thermodynamically unfavorable. However, it is clear that $[Fe(NTA)DBC]^{2-}$ reacts with dioxygen.

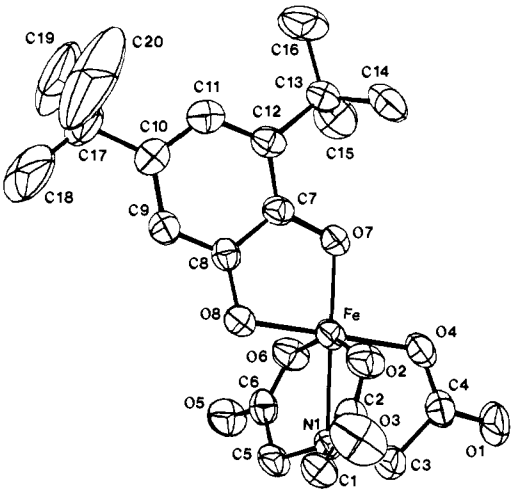

Figure 1. Structure of $[Fe(NTA)DBC]^{2-}$ showing 50% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms omitted for clarity. Selected bond distances in Å: Fe–N1, 2.224 (3); Fe–O2, 2.034 (3); Fe–O4, 2.002 (3); Fe–O6, 2.039 (3); Fe–O7, 1.887 (3); Fe–O8, 1.979 (3).

The structure of the $[Fe(NTA)DBC]^{2-}$ complex suggests a possible explanation for its reactivity. Crystallographic quality crystals can be obtained from anaerobic DMF solutions containing stoichiometric amounts of Fe(NTA), $DBCH_2$, and dabco. $(dabcoH)_2[Fe(NTA)DBC]\cdot DMF$ crystallizes as hexagonal plates in the space group $P2_1/n$.[12] Refinement of the data yields an ORTEP plot of the anionic complex shown in Figure 1. The complex is a distorted octahedron featuring a tetradentate NTA and a bidentate catecholate. The most striking feature of this structure is the significant difference in the two Fe–O(DBC) bond lengths—1.887 (3) and 1.979 (3) Å. By comparison, the Fe–O(catechol) bonds in $[Fe(salen)cat]^-$ are both 1.99 Å long[13] and the Fe–O bonds in $[Fe(cat)]_3^{3-}$ show a range of 2.00–2.04 Å.[14] Steric effects are not responsible for the different bond lengths in $[Fe(NTA)DBC]^{2-}$; indeed, the DBC oxygen proximal to the 3-*tert*-butyl group, has the shorter Fe–O bond. Close examination of the structure reveals the source of this large difference: the shorter Fe–O bond is trans to the Fe–N bond. Due to the constraints on the NTA ligand required by its tetradentate ligation, the Fe–N bond is 2.224 (3) Å, which is longer than those in less constrained complexes such as $[Fe(acac)_2trien]^+$ (2.175 Å),[15]

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(9) Abbreviations used: NTA, nitrilotriacetate; $DBCH_2$, 3,5-di-*tert*-butylcatechol; salen, *N*,*N*′-ethylenebis(salicylideneamine); DBSQ, 3,5-di-*tert*-butyl-*o*-benzosemiquinone anion; dabco, 1,4-diazabicyclo[2.2.2]octane; $catH_2$, catechol; Hacac, 2,4-pentanedione; trien, triethylenetetraamine; EHPG, *N*,*N*′-ethylenebis(*o*-hydroxyphenylglycine) tetraanion; tacn, 1,4,7-triazacyclononane; OAc, acetate; EDTA, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate; pip, piperidine.

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(12) $(dabcoH)_2[Fe(NTA)DBC]$ crystallizes in the monoclinic system, space group $P2_1/n$, with a = 17.874 (4) Å, b = 9.963 (3) Å, c = 23.117 (9) Å, β = 105.38 (3)°, V = 3969.3 Å^3, ρ_{obsd} = 1.28 g cm^{-3}, ρ_{calcd} = 1.278 g cm^{-3}, and Z = 4. With the use of 3413 unique observed reflections collected at 298 K with Mo K$\bar{\alpha}$ (λ = 0.7107 Å) radiation out to 2θ = 48° on an Enraf-Nonius CAD4 X-ray diffractometer, the structure was solved by Patterson and Fourier methods and refined anisotropically to a final value for the discrepancy index R_1 of 0.067. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

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