Heteroatom Exchange Reactions in Imidoosmium(II) Systems: Cleavage of Os–N Multiple Bonds and Formation of Os–X Bonds (X = O, S, C)

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The monomeric imido complex CymOsN-*t*-Bu (**2**) (Cym = η^6-*p*-cymene) was used as a convenient precursor in exchange reactions with a variety of H–X bonds (X = O, S, C). Complex **2** reacts with alkoxides $HOCMe(CF_3)_2$, pinacol, catechol, and 1,2-$(H_2N)(HO)C_6H_4$ to give CymOs(NH-*t*-Bu)[$OCMe(CF_3)_2$] (**4**), CymOs[$OC(CH_3)_2C(CH_3)_2O$] (**5**), CymOs[1,2-$O_2C_6H_4$] (**6**), and CymOs[1,2-$O(HN)C_6H_4$] (**7**), respectively. CymOs(O-*t*-Bu)$_2$ (**3**) was not formed by this method but was generated by treatment of $[CymOsCl_2]_2$ (**1**) with KO-*t*-Bu. Addition of H_2N-*t*-Bu to **3** gave **2**, and reaction of **5** with catechol gave **6**. Complex **6** adds PMe_3 to give CymOs[1,2-$O_2C_6H_4$](PMe_3) (**8**). Catechol, 1,2-$(H_2N)_2C_6H_4$, or H_2N-*p*-tol hydrogen bond or coordinate to the metal in **6** or CymOs[1,2-$(NH)_2C_6H_4$] (**10**). Reactivity patterns generally correlate with the pK_a of the substrate, but other factors are also involved. Several analogous thiolate complexes were also prepared. For example, imido complex **2** or bis(*tert*-butoxide) **3** reacted readily with *t*-Bu–SH to give CymOs(S-*t*-Bu)$_2$ (**13**). The analogous osmium complexes with 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$ groups attached to the sulfur atoms (**14** and **15**, respectively) were obtained by treatment of imido complex **2** with the appropriate thiols. However, reaction of **2** with *p*-tol–SH gave the dimeric thiolate complex $[CymOs(S\text{-}p\text{-}Me\text{–}C_6H_4)_2]_2$ (**16**). Complex **2** also reacts with carbon acids. The more acidic C–H bond of $H_2C(COMe)_2$ (acacH) caused the addition of 2 mol of diketone with *tert*-butylamine loss to give CymOs[$CH(COMe)_2$][$(OC(Me))_2CH$-*O,O*] (**18**) whereas the weaker acid ($H_2C(CO_2Me)_2$) added only once across the Os–N bond to give CymOs(NH-*t*-Bu)[$CH(CO_2Me)_2$] (**17**). Treatment of dichloro dimer $[CymOsCl_2]_2$ with K_2CO_3 and acacH quantitatively provided yellow CymOs(acac-*O,O*)Cl (**19**). Monoacetylacetonato complex **19** was treated with AgOAc (Ac = COMe) to give CymOs(acac)(OAc) (**21**). Dimethyl malonate complex **17** was independently treated with acacH and $H_2C(CO(Ph))_2$ to give CymOs[$CH(CO_2Me)_2$][$(OC(Me))_2CH$] (**22**) and bright red CymOs[$CH(CO_2Me)_2$][$(OC(Ph))_2CH$] (**23**). Carbon–proton NMR coupling data provided evidence for the presence of carbon–metal bound diketonate ligands in **17**, **18**, **22**, and **23**.

Introduction

Late transition metal complexes with M–X bonds (X = O, N, S)[1-5] are critical intermediates in many catalytic processes,[1,6] such as hydrodesulfurization,[7] hydrodeamination,[8,9] and catalytic cracking.[10] The preparation and direct study of these species enables a thorough investigation of their properties, including relative bond strengths.

The imido complex CymOsN-*t*-Bu (**2**) (Cym = η^6-*p*-cymene)[11] is a convenient precursor to such metal–heteroatom species, as well as metal–carbon bonded compounds.[12,13] σ-Ligand metathesis reactions with **2** have enabled us to study complexes of this type, many of which are formally unsaturated. We report here the full details of this work.[14]

Results

Synthesis of Osmium Alkoxide Complexes. The alkoxide complexes described in this paper were synthesized using the CymOs fragment (Cym = η^6-*p*-cymene) as outlined in Scheme 1. Treatment of $[CymOsCl_2]_2$ (**1**) with 3 equiv of KO-*t*-Bu in THF yielded the deep-red bis(alkoxide) compound CymOs(O-*t*-Bu)$_2$ (**3**) in 47% yield. Although this complex was characterized spectroscopically, its instability in the solid state (decomposition results in the formation of *p*-cymene and intractable materials) prevented adequate microanalysis. This material was therefore used immediately after formation. Attempted

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(12) For a review of transition metal imido chemistry, see: Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

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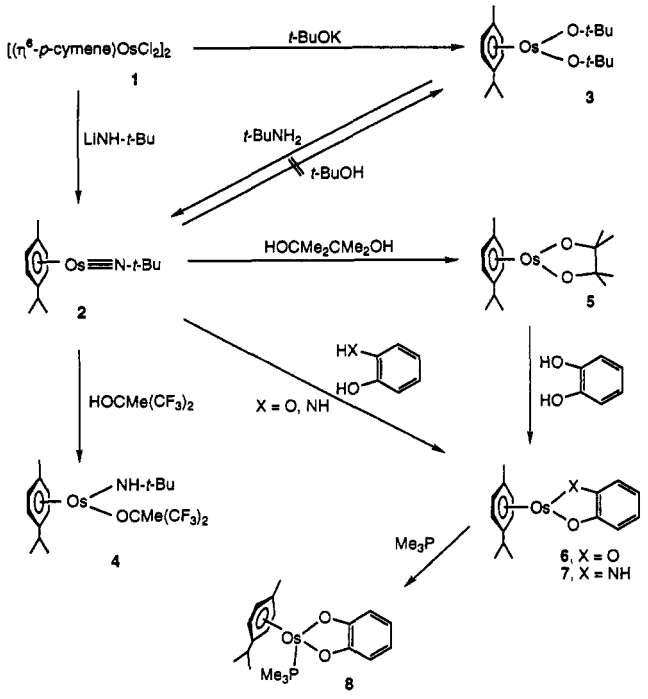
Scheme 1



purification by sublimation or chromatography on silica gel or alumina III was unsuccessful. Compound **3** did not react with the donor ligands (*N*,*N*-dimethylamino)pyridine or PMe_3, and it decomposed upon addition of XylNC (Xyl = 2,6-$Me_2C_6H_3$). Reactions of **1** with LiO-*t*-Bu or NaO-$SiMe_3$ resulted in formation of intractable materials.

Treatment of a C_6D_6 solution of bis(alkoxide) **3** with 1 equiv of H_2N-*t*-Bu resulted in rapid generation of CymOsN-*t*-Bu (**2**). Imido complex **2** can be prepared directly from **1** and LiNH-*t*-Bu.[11,14] Free HO-*t*-Bu was observed in the reaction solution by ^1H NMR spectroscopy, and no osmium-containing starting material remained.

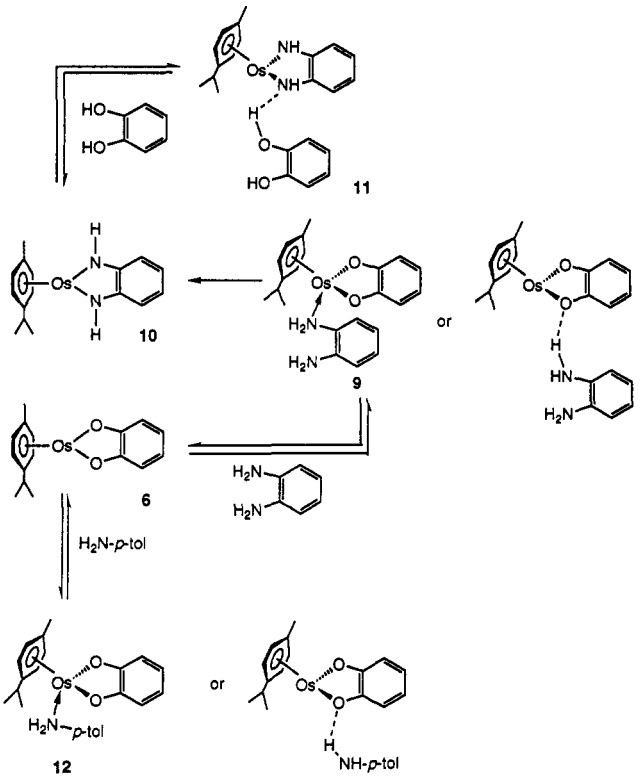
No **3** was observed in the ^1H NMR spectra from +21 to −89 °C when 3.4 equiv of HO-*t*-Bu and **2** were mixed in toluene-d_8. Treatment of **2** with the more acidic alcohol $HOCMe(CF_3)_2$, however, gave the red-orange oil CymOs(NH-*t*-Bu)[$OCMe(CF_3)_2$] (**4**) in 87% yield. This product exhibits NH resonances at δ 11.07 and *tert*-butyl proton signals at δ 1.13 in the ^1H NMR spectrum. The $^{13}C\{^1H\}$ NMR resonances at δ 6.10 and 32.1 are consistent with the *tert*-butyl group, and resonances at δ 125.9 (quart) and 80.3 (sept) showed coupling to the ^{19}F of the $OCMe(CF_3)_2$ group (J_{HF} = 291.7 Hz and 27.0 Hz, respectively). The $^{19}F\{^1H\}$ NMR spectrum of **4** shows only one resonance, at δ −77.8. No line shape changes were observed in the ^1H and $^{19}F\{^1H\}$ NMR spectra from +44 to −73 °C. The N–H stretch was not observed in the infrared spectrum of **4**. The reaction of $LiOCMe(CF_3)_2$ with $CymOs(NH_2$-*t*-Bu)Cl_2 (generated as a metastable species by addition of *tert*-butylamine to $[CymOsCl_2]_2$) gave a mixture of products, none of which were **4**.

Chelating Alkoxide Complexes. Pinacol ($HOC(CH_3)_2C(CH_3)_2OH$) reacted with imide **2** to give red $CymOs[OC(CH_3)_2C(CH_3)_2O]$ (**5**) in >98% yield by ^1H NMR spectroscopy. The compound was isolated as needles from Et_2O in 34% yield. The pinacolate complex **5** is much more robust than bis(alkoxide) **3**, and it is isolable at room temperature. Complex **5** was inert to photolysis and thermolysis, showing no C–C bond cleavage products, as was observed for analogous complexes of Ru, Rh, and Pt.[15-17]

Imide **2** reacted with 1 equiv of catechol ($1,2\text{-}(HO)_2C_6H_4$) at room temperature to yield red $CymOs[1,2\text{-}O_2C_6H_4]$ (**6**) in 69% yield. Complex **6** was also formed in 59% yield from **5** and 1.25 equiv of catechol. On treatment with $1,2\text{-}(H_2N)(HO)C_6H_4$, **2** gave $CymOs[1,2\text{-}O(HN)C_6H_4]$ (**7**) in 99% yield, which exhibits an NH resonance at δ 8.68 in the ^1H NMR spectrum and an N–H stretch at 3342 cm^{-1} in the IR spectrum. Catecholate **6** formed an adduct with PMe_3, $CymOs[1,2\text{-}O_2C_6H_4](PMe_3)$ (**8**), in 99% yield. This complex shows a single $^{31}P\{^1H\}$ NMR resonance at δ −23.3.

The addition of 1,2-diaminobenzene to **6** resulted in the formation of an adduct **9** (Scheme 2). No free **6** was

Scheme 2



observed in the product solution, and the resonances for the *p*-cymene and catecholate ligands appeared in the ^1H NMR spectrum at different chemical shifts than those observed for **6**. In addition, the resonances for the diamine are broadened. This indicates that the diamine is coordinated to **6**, and two possible coordination modes are shown in Scheme 2 (Os–N coordination and hydrogen bonding). The room temperature spectrum is an averaged one. When the solution was heated at 45 °C for 19 h, $CymOs[1,2\text{-}(NH)_2C_6H_4]$ (**10**)[11] was obtained in 98% yield, as determined by ^1H NMR spectroscopy.

The reverse reaction was investigated by treating **10** with 2.8 equiv of catechol at room temperature (Scheme 2). This returned mostly **10**, and the new complex **11** as observed by separate resonances in the ^1H NMR spectrum (3:2). The structure of **11** is likely to be a hydrogen-bonded

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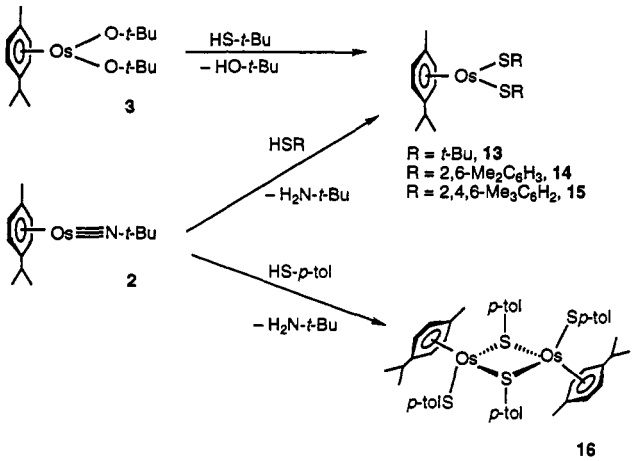
complex. Similar species exist with Cp*Rh catecholates.[18] At higher temperatures (+77 °C) the ^{1}H NMR spectrum shows only **10**, whereas the bound-catechol complex **11** is formed exclusively at −42 °C. Interestingly, no **11** was observed in the conversion of **9** to **10**. This is presumably due to both the lower concentration of catechol in the **9** to **10** reaction (1 equiv of catechol to 1 equiv of **10**) vs the direct reaction of **10** and catechol above (2.8 equiv of catechol to 1 equiv of **10**), and the presence of excess 1,2-diaminobenzene in the **9** to **10** conversion.

Catecholate **6** also forms a complex with H_2N-*p*-tol (Scheme 2). The 1:1 complex **12** shows variable temperature behavior in the ^{1}H NMR spectrum. The two aromatic *p*-cymene resonances change in chemical shift by 0.60 and 0.71 ppm as the temperature is varied from −55 to +90 °C. The NH_2 resonance moves from δ 4.20 at −5 °C to δ 2.81 at +90 °C but is not observed at temperatures lower than −5 °C. The two sides of the catecholate ligand do not show asymmetry at lower temperatures, though the possibility of rapid exchange precludes a definitive structural assignment.

Reactions of **2** with other alcohols were less successful. Treatment of **2** with isopropanol resulted in the formation of several unstable products, as observed by ^{1}H NMR spectroscopy. Reactions with HO-*p*-tol or HO(2,6-$Me_2C_6H_3$) generated single complexes that were stable in solution but decomposed to intractable materials when the solvent (C_6D_6) was lyophilized. The reaction of **2** with water proceeded slowly (and only with partial conversion) to intractable materials.

Thiolate Complexes. Exchange reactions of imido complex **2** with thiols were rapid (<45 min) (Scheme 3).

Scheme 3



Treatment of **2** with HSR (R = *t*-Bu, 2,6-$Me_2C_6H_3$ (Xyl), 2,4,6-$Me_3C_6H_2$ (Mes)) gave the violet (bis)thiolate complexes CymOs(S-*t*-Bu)$_2$ (**13**), CymOs(SXyl)$_2$ (**14**), and CymOs(SMes)$_2$ (**15**) in 83–94% yield. Complex **13** was also synthesized from **3** and HS-*t*-Bu. Free H_2N-*t*-Bu and HO-*t*-Bu were observed in the ^{1}H NMR spectra of the reaction solutions from **2** and **3** with HS-*t*-Bu, respectively. Variable temperature ^{1}H NMR spectra of **13** from +25 to −88 °C showed only one type of *tert*-butyl resonance, indicating that either only a monomer is present in solution or bridge–terminal exchange in a dimer or higher oligomer is rapid.[19] Two different thiolate signals (bridging and terminal) were observed in the room temperature ^{1}H NMR

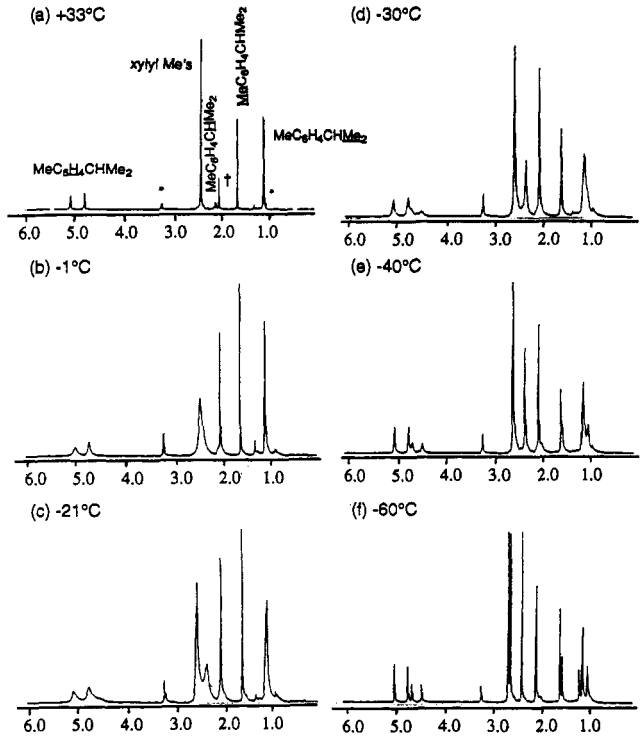
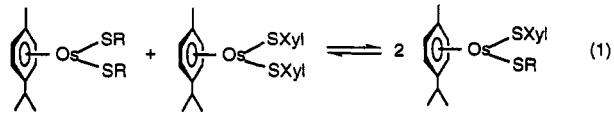


Figure 1. ^{1}H NMR spectra of **14** in toluene-d_8 from +33 to −60 °C (0–6 ppm region only). Et_2O is marked with *, and the methyl resonance of the solvent is marked with †.

spectrum of the dimer [CymOs(S-*p*-tol)$_2$]$_2$ (**16**), prepared from **2** and HS-*p*-tol (Scheme 3), and it is therefore reasonable to postulate that **13** is a monomer. Unfortunately, **16** decomposed slowly in the solid state to intractable materials, so further characterization was not possible.

Arenethiolate complexes **14** and **15** showed similar variable temperature ^{1}H NMR behavior (Figure 1). The 33 °C spectrum of **14** in toluene-d_8 (Figure 1a) showed resonances for a single compound, consistent with CymOs(SXyl)$_2$. Cooling **14** to −21 °C (Figure 1c) resulted in decoalescence of both the Cym and the SXyl resonances. Resonances for two complexes (2:1) were apparent in the spectrum at −40 °C (Figure 1e). Further cooling to −60 °C (Figure 1f) showed no change in the ratio of the two species (as monitored by the *p*-cymene resonances), but the xylyl resonances for the dominant species split into two different resonances (1:1). The −65 °C spectrum of **15** showed similar features. Concentration and solvent dependence studies of **15** showed no significant change in the ratio of the two species at −65 °C (Table 1).

Crossover experiments were run with **14** and **15**. The two complexes were mixed in C_6D_6, and $^{13}C\{^1H\}$ and DEPT NMR spectra[19] showed a 1:2:1 ratio of **14**, a new material that presumably is CymOs(SXyl)(SMes), on the basis of chemical shifts (Figure 2), and **15** (eq 1). A similar



(1)

R = *t*-Bu (**13**)
R = 2,4,6-$Me_3C_6H_2$ (**15**) **14**

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Table 1. ^{1}H NMR Sample Data for Experiments with 15 at −65 °C

[15] (mM)	solvent	ratio of compounds[a]
6.1	toluene-d_8	2.0:1
21	toluene-d_8	1.9:1
6.1	CD_2Cl_2	2.1:1

[a] Based on integration of aromatic *p*-cymene resonances.

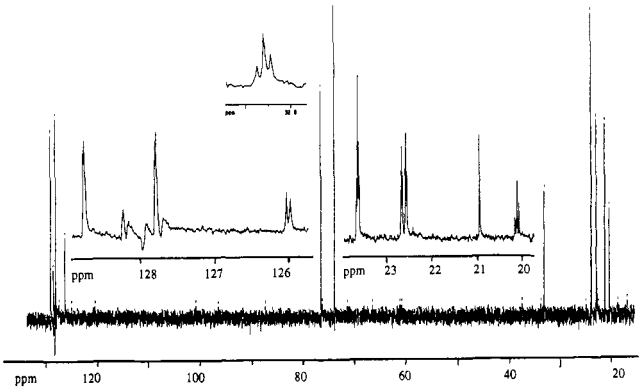

Figure 2. DEPT135 spectrum of the reaction mixture of **14** and **15** in C_6D_6 with expansions.

experiment with **13** and **14** showed resonances for the expected mixed product CymOs(S-*t*-Bu)(SXyl) (or possibly the dimer) in the ^{1}H NMR spectrum.

Reactions of 2 with Carbon Acids. Treatment of **2** with 1 equiv of dimethyl malonate ($H_2C(CO_2Me)_2$) gave the dark-red compound CymOs(NH-*t*-Bu)[$CH(CO_2Me)_2$] (**17**) in 85% yield (Scheme 4). When 2 equiv of $H_2C(CO_2Me)_2$ was added to **2**, no further reaction was observed. The use of 1 equiv of $D_2C(CO_2Me)_2$ yielded CymOs(ND-*t*-Bu)[$CD(CO_2Me)_2$] (**17**-d_2), which allowed the resonances for NH to be assigned at δ 13.20 and CH at δ 4.83 in the ^{1}H NMR spectrum. The infrared spectrum for **17** displays an N–H stretch at 3261 cm^{-1}; the N–D stretch was observed at 2425 cm^{-1} in the spectrum of **17**-d_2. The coupled ^{13}C NMR spectrum of **17** shows a doublet at δ 36.7 with J_{CH} = 138 Hz for the methine carbon. This is consistent with sp^3 hybridization at the carbon center. Table 2 shows chemical shifts and coupling constants of compounds derived from carbon acids that were prepared in this work. The ^{13}C chemical shifts of the Os–$CH(CO_2Me)_2$ fall in the range 31–58 ppm with $J \approx 140$ Hz, whereas those that are oxygen bound fall at higher δs with $J \approx 160$ Hz. An inverse H–C correlated NMR (HMQC) spectrum[20] of the cross

Scheme 4

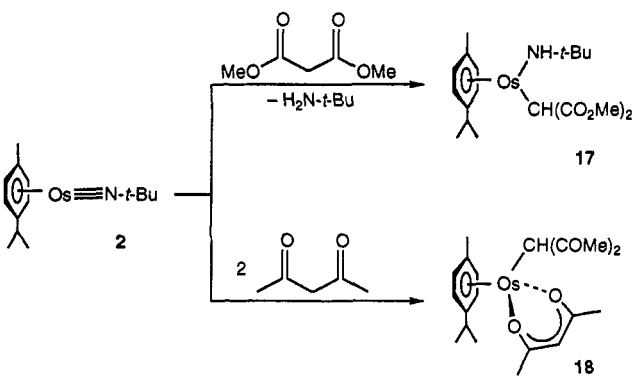

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Table 2. ^{1}H and ^{13}C NMR Chemical Shifts (δ), C–H Coupling Constants (J_{CH}), and Hybridization for Carbon Acid Complexes 17–23

compd	bonding mode[a]	C–H δ (ppm)[b] ^{1}H	^{13}C	J_{CH} (Hz)	hybridization
17	1	4.83	36.7	138	sp^3
18	2	5.12	101.3	159	sp^2
	1	4.61	57.7	134	sp^3
19	2	5.14	100.7	160	sp^2
20	2	6.65	95.8	158	sp^2
21	2	5.08	99.7	159	sp^2
22	2	5.10	100.9	159	sp^2
	1	4.17	31.1	138	sp^3
23	2	6.63	113.3	158	sp^2
	1	4.47	31.7	138	sp^3
Cp*Ir(acac)Cl[21,c]	2	5.19			
Cp*Ir(acac)$_2$[21,c]	2	5.20			
	1	4.74			
CymRu(acac)Cl[22,c]	2	5.11			

[a] 1 = unidentate, *C*-bound; 2 = bidentate, *O,O*-bound. [b] All spectra recorded at 25 °C in C_6D_6 (except as in *c*). [c] Spectra recorded in $CDCl_3$.

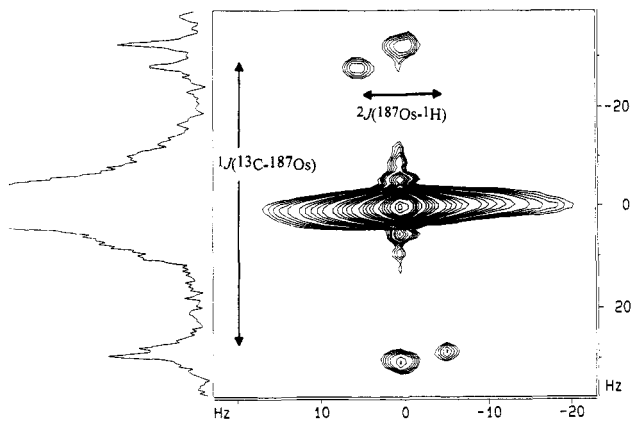
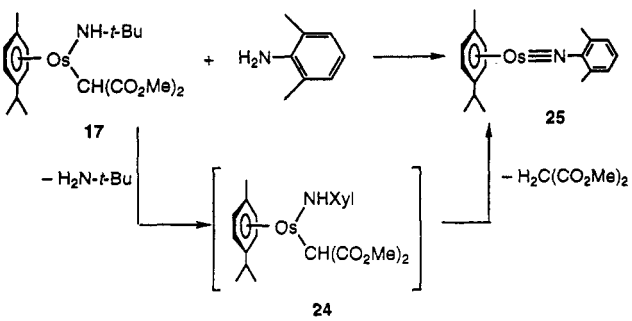


Figure 3. Inverse H–C correlated NMR spectrum of **17** showing only the osmium bound C–H resonance: vertical dimension ^{13}C, annotated with the normal ^{13}C{^{1}H} NMR spectrum; horizontal dimension ^{1}H.

peak due to the carbon resonance that appears at 36.7 ppm and the proton resonance at 4.83 ppm displays satellites for ^{187}Os–^{13}C and ^{187}Os–^{1}H coupling (Figure 3), verifying the Os–C connectivity ($^1J_{OsC}$ = 56.6 Hz; J_{OsH} = 10.6 Hz).

Treatment of **17** with 2.6 equiv of H_2NXyl gave new resonances in the ^{1}H NMR spectrum after 30 min which were consistent with CymOs(NHXyl)[$CH(CO_2Me)_2$] (**24**) in 33% yield (Scheme 5). Addition of more amine produced CymOsNXyl (**25**)[11,14] (83% yield), along with H_2N-*t*-Bu and $H_2C(CO_2Me)_2$, as verified by ^{1}H NMR spectroscopy. The reverse reaction with **25** and 6 equiv of $H_2C(CO_2Me)_2$ did not give **24**. No isolable products were formed from the reaction of **17** and PPh_3, PMe_3, XylNC, or I_2.

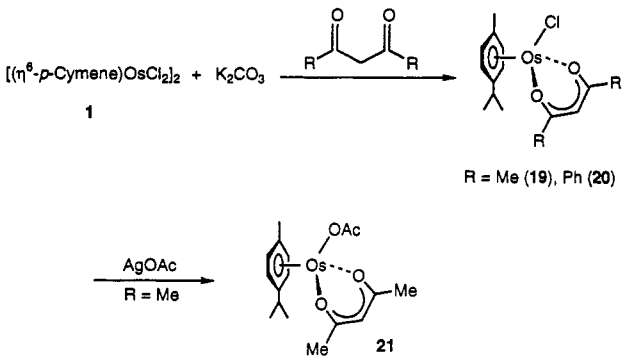
Scheme 5



Addition of 2 equiv of $H_2C(COMe)_2$ (acacH) to **2** resulted in the formation of yellow CymOs[CH(COMe)$_2$-*C*][(OC(Me))$_2$CH-*O,O*] (CymOs(acac)$_2$, **18**) in 74% yield (Scheme 4). The coupled ^{13}C NMR spectrum of **18** showed resonances with J_{CH} = 159 Hz (δ 101.3) and 134 Hz (δ 57.7) for the methine carbon on the *O,O*-bound acac ligand and C-bound acac ligand, respectively (Table 2). The carbonyl absorption for the C-bound acac appears at 1678 cm^{-1} in the infrared spectrum. No resonances for CymOs(NH-*t*-Bu)[*C*-CH(COMe)$_2$] or CymOs(NH-*t*-Bu)[(OC(Me))$_2$CH-*O,O*] were observed by ^1H NMR spectroscopy when **2** was treated with 1 equiv of acacH, but 0.5 equiv of **18** was formed instead.

Treatment of dichloro dimer **1** with K_2CO_3 and acacH quantitatively provided yellow CymOs(acac-*O,O*)Cl (**19**) (Scheme 6). Addition of 2 equiv of acacH and K_2CO_3 to

Scheme 6



1 only gave **19**; no **18** was observed. The coupled ^{13}C NMR spectrum of **19** showed J_{CH} = 160 Hz at δ 100.7 for the acac methine carbon, indicating that the (OC(Me))$_2$CH ligand is O,O-bound, and the methine carbon is sp^2 hybridized. The similar diphenyl diketonato complex CymOs[(OC(Ph))$_2$CH-*O,O*]Cl (**20**) (Scheme 6), prepared in 57% yield from **1**, K_2CO_3, and $H_2C(CO(Ph))_2$, shows J_{CH} = 158 Hz. Neither **19** nor **20** shows a carbonyl stretch in the IR at frequencies higher than 1600 cm^{-1}. The synthesis of CymOs[CH(CO$_2$Me)$_2$]Cl (O,O- or C-bound) was not successful with $H_2C(CO_2Me)_2$, K_2CO_3, and **1**.

Monoacetylacetonato complex **19** was treated with AgOAc (Ac = COMe) to give CymOs(acac)(OAc) (**21**) in 94% yield (Scheme 6). This compound showed a typical carbonyl absorption for OAc and J_{CH}(acac) = 159 Hz obtained from the ^{13}C satellites in the ^1H NMR spectrum. Complex **19** did not react with Li(acac), KCH(COPh)$_2$, or KO-*t*-Bu, while **21** decomposed to intractable products in the presence of KCH(COPh)$_2$. Complex **19** did, however, react with 6 equiv of LiNH-*t*-Bu to give imide **2**.

Dimethyl malonate complex **17** was independently treated with acacH and $H_2C(CO(Ph))_2$ to give yellow CymOs[CH(CO$_2$Me)$_2$][(OC(Me))$_2$CH] (**22**) and bright red CymOs[CH(CO$_2$Me)$_2$][(OC(Ph))$_2$CH] (**23**) in 90% and 58% yields, respectively (Scheme 7). The malonate–diketone complexes exhibit the chemical shift and coupling constant data shown in Table 2. As discussed above for the other complexes listed in Table 2, these data rule out alternative structures such as CymOs[(OC(OMe))$_2$CH-*O,O*][CH(COR)$_2$-*C*] (R = Me, Ph).

Interestingly, only intractable materials were recovered from the reaction of **2** with $H_2C(CO(Ph))_2$. The reaction appeared to first give a complex with NH-*t*-Bu and CH(COPh)$_2$ groups, as seen in the ^1H NMR spectrum, before

Scheme 7

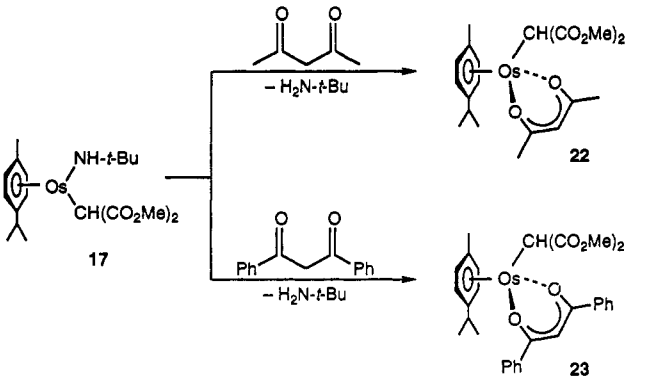


Table 3. pK_a Data for Several Heteroatom Compounds

heteroatom reagent	pK_a (DMSO)[28]
PhSH (ArSH)	10.3
n-BuSH (*t*-BuSH)	17.0
PhOH	18.0
$PhNH_2$ ($XylNH_2$)	30.6
t-BuOH	32.2

decomposing in solution (free *p*-cymene was observed). No reaction occurred between **2** and PhCOMe, as observed by ^1H NMR spectroscopy.

Discussion

Imide/Alcohol and Imide/Thiol Exchange Reactions with Imide 2. In contrast to the inert M–N linkages in most transition metal imido complexes,[12,21] the d^6 osmium(II) species CymOsN-*t*-Bu (**2**) reacts readily with a variety of H–X bonds (X = O, S, C). In most cases, this involves cleavage of the osmium–nitrogen triple bond.[11,22,23] These σ-ligand metathesis reactions[1,24–27] are general and usually occur rapidly at room temperature to give CymOs(XR)$_2$. The stability of these species is dependent on the nature of the substituent (X) bonded to the metal as well as R.

Reactions proceeded forward from **2** when it was treated with proton–heteroatom bonded reagents HXR such as alcohol $HOCMe(CF_3)_2$ to give **4**, diols pinacol and catechol to give **5** and **6**, and amino alcohol 1,2-(HO)(H$_2$N)C$_6$H$_4$ to give **7** (Scheme 1). Thiols HS-*t*-Bu, HSXyl, HSMes, and HS-*p*-tol reacted to give **13**, **14**, **15**, and **16** (Scheme 3), and previous work with **2** has demonstrated that the reaction is successful with amines H_2NXyl and 1,2-diaminobenzene, giving **25** and **10**, respectively.[11,14]

The reactions with protic acids appear to depend, at least partially, on pK_a (Table 3). The thiols employed, with pK_a values of 17 or less in DMSO,[28] react with imide **2** to give CymOs(SR)$_2$, while HO-*t*-Bu (pK_a = 32.2) does not react (the pK_a of $PhNH_2$ is 30.6, and that of H_2N-*t*-Bu will be higher). The alcohol $HOCMe(CF_3)_2$ is more acidic

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(22) Glueck, D. S.; Wu, J.; Hollander, F. W.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.
(23) Glueck, D. S.; Green, J. C.; Michelman, R. I.; Wright, I. N. *Organometallics* **1992**, *11*, 2441.
(24) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.
(25) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805 and references therein.
(26) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939.
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than HO-*t*-Bu due to the electron-withdrawing fluorines, and gives the mono-exchange product **4** when added to **2**. The complex CymOs[$OCMe(CF_3)_2$]$_2$ was not observed, despite the presence of additional alcohol in reaction solutions of **4**. The reaction may not proceed from the mixed compound **4** because of the stabilizing effects offered by NH-*t*-Bu over $OCMe(CF_3)_2$, perhaps due to NH-*t*-Bu being a better π-donor than $OCMe(CF_3)_2$. The 16-electron osmium center has empty orbitals for use in π-bonding with the nitrogen p-orbital, thus strengthening the Os—N bond. In the hypothetical bis(alkoxide) complex, the two $OCMe(CF_3)_2$ ligands would be required to compete for the Os orbital and presumably destabilize the complex. The preceding argument has been invoked in Mo=O bonding.[29]

An approximate acidity comparison between the diols pinacol (pK_a of *t*-BuOH = 32) and catechol (pK_a of PhOH = 18) accounts for the fact that treatment of pinacolate **5** with catechol yields catecholate **6** and pinacol (Scheme 1). Another example involves the treatment of bis(alkoxide) **3** with HS-*t*-Bu ($pK_a \approx 17$) to give (bis)thiolate **13** and HO-*t*-Bu (pK_a = 32.2). However, there are inconsistencies with the acidity guideline for predicting the direction of these exchange reactions. In a 1:1 exchange, the less acidic 1,2-$(H_2N)_2C_6H_4$ (based on $PhNH_2$ (pK_a = 30.6) and PhOH (pK_a = 18.0)) displaces catechol from **6**, but the back-reaction was not observed. Similarly, *tert*-butylamine successfully replaced 2 equiv of *tert*-butanyl alcohol from **3**, generating **2**.

The direction of reactions we have observed for the σ-ligand metathesis reactions must depend on both pK_a's and metal–ligand ionic dissociation energies, as shown in eqs 2–6. For example, the equilibria giving rise to the pK_a

$$RNH_2 \rightleftharpoons RNH^- + H^+ \quad (2)$$

$$H^+ + OR^- \rightleftharpoons H\text{–}OR' \quad (3)$$

$$M\text{–}OR' \rightleftharpoons M^+ + OR^- \quad (4)$$

$$M^+ + NHR^- \rightleftharpoons M\text{–}NHR \quad (5)$$

$$RNH_2 + M\text{–}OR' \rightleftharpoons H\text{–}OR' + M\text{–}NHR \quad (6)$$

values for an alkoxide and an amine are shown in eqs 2 and 3. Only if the ionic dissociation energies of M–OR′ (eq 4) and M–NHR (eq 5) were equal would the simple pK_a values control the direction of exchange. The fact that some of the exchange equilibria do not correlate with the relative pK_a's of the organic reaction partners requires that the energies of eqs 4 and 5 can work in opposition to eqs 2 and 3. Thus in the conversion of **6** to **10**, the Os–N ionic dissociation energy must be greater than that for Os–O, such that the difference in pK_a between the diol and the diamine is overcome.

We do not know the mechanism of these reactions, but the imide/alcohol and imide/thiol exchange reactions may be initiated by either hydrogen bonding to the imido nitrogen or by metal complexation of the entering reagent. Hydrogen bonding or coordination could facilitate subsequent transfer of a proton to the leaving ligand. The latter option is similar to the mechanism proposed for imide/amine exchange, in which a deuterium isotope effect of 5.7 was observed.[11] The difficulty in differentiating between hydrogen bonding and precoordination to the metal in complexes **9**, **11**, and **12** makes the prediction of reactivity more intricate because the barrier to proton transfer may be substantially modified by complexation of the incoming reagent to the osmium center.

It is important to consider these possibilities when looking at related systems.[3,30] Several rhodium catecholates,[18] prepared earlier with catechol and aqueous base, are isolated with associated water molecules. The structure of one of these compounds shows hydrogen bonding of catechol in the solid state to the oxygens of the catecholatorhodium fragment. Maitlis suggested that the additional species (H_2O or catechol, as determined by analytic and spectroscopic methods) attached to the catecholate ligand are necessary to stabilize the crystal lattice.[18] These compounds retain bound H_2O when phosphine adducts are formed, but the phosphines are labile. In contrast, we have found that the osmium catecholate **6** can be generated from **2** without excess catechol or water, as can CymOs[1,2-$O(NH)C_6H_4$] (**7**) and CymOs[1,2-$(NH)_2C_6H_4$] (**10**).[11] Reaction of **6** with phosphine gave **8**, which is a donor complex. A fluxional process similar to that observed in the Cp*Rh complexes would explain the difficulty in observing the quaternary *p*-cymene carbons in the $^{13}C\{^1H\}$ NMR spectrum of **8**.

Similar to the Cp*Rh complexes[18] and other late metal phenoxide complexes,[31,32] catechol is likely to be hydrogen bonded in CymOs[1,2-$(NH)_2C_6H_4$]·$(HO)_2C_6H_4$ (**11**). Coordination of N to Os in the amine complexes **9** and **12** is reasonable, on the basis of the formation of **8** with phosphine. However, we cannot definitively assign the bonding mode for the amine compounds. Maitlis does suggest, however, that the Rh–N bond is stronger than the Rh–O bond. Our results with Os–N vs Os–O agree with this hypothesis, as observed in the ligand exchange of **6** to **10** with 1,2-diaminobenzene. The O–H bond in phenol and the N–H bond in aniline are about equal in energy, 87 and 88 kcal/mol, respectively.[33] Assuming the effects of disubstitution on the aromatic rings (HXC_6H_5 vs $(HX)_2C_6H_4$) are similar for X = O and NH, the Os–N bond must be stronger.

Entropy also plays a critical role in the reactions of **2** with alcohols *tert*-butyl alcohol and pinacol. No reaction was observed when imido complex **2** was treated with HO-*t*-Bu, suggesting $\Delta G > 0$ for the imide to bis(alkoxide) reaction. Further investigation of this reaction by low temperature (−89 °C) ^1H NMR spectroscopy did not show resonances for **3**, as might be expected if ΔS was preventing this reaction from proceeding at room temperature. However, the pinacolate **5** and *tert*-butylamine were readily formed from **2** and pinacol (Scheme 1). This difference between the reactivity of HO-*t*-Bu and pinacol with **2** is best explained by the chelate effect.[6]

Structures of the 16-Electron Complexes CymOs(XR)$_2$ (X = O, S). The bis(alkoxide) complexes **3**, **5**, and **6**, as well as the mixed amide/alkoxide complexes **4** and **7**, would be 16-electron, d^6 metal compounds as monomers,

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(33) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

which are uncommon for the (arene)Os fragment.[13] Although we have not been successful in obtaining crystal structures of these materials, mononuclear structures are proposed on the basis of comparison with other similar structurally characterized complexes.[1,2,17,34,35] Furthermore, thiolates are more prone to bridge than alkoxides due to their larger size (van der Waals radii).[36] By analogy with monomeric bis(*tert*-butanethiolate) **13** (see below), bis(*tert*-butoxide) **3** is likely to be mononuclear, although its instability precluded further studies.

There is a relatively small, but growing, number of late transition metal alkoxide complexes.[1] With respect to unsaturated compounds, a case has recently been made that π-donation of electron density from alkoxide ligands to ruthenium[37] and iridium[38] stabilizes the metal centers. A similar effect may be important in the osmium compounds described here, but there are no spectroscopic data to confirm this. It is significant, however, that the 16-electron alkoxide complex **3** does not react with donor ligands such as PMe_3, particularly since the stable complex $Cp^*Ir(PMe_3)(S\text{-}t\text{-}Bu)_2$ is known.[39] The better π-donating ability of oxygen vs sulfur is consistent with this observation.

The C–C bond cleavage observed with some late-metal pinacolate complexes[15–17,35] did not occur with **5** upon photolysis or thermolysis. Apparently, these processes are not favored for the third-row d^6 metal Cp*Ir and CymOs centers.

The monomeric nature of bis(*tert*-butanethiolate) **13** is strongly supported by the accessibility of dimer **16**, which has a clearly distinguishable NMR spectrum. The room temperature ^1H NMR spectrum of **16** exhibits two types of S–*p*-tolyl groups, which are most directly assigned to those in the terminal and bridging positions. The compound was not obtained pure so this inequivalence must be considered tentative at present. However, it provides evidence that if **13** were dimeric, it would have to have either a substantially different structure or rapidly exchanging thiolate groups.

The nuclearity of arenethiolates **14** and **15** is less clear. The gas phase mass spectral data for **15** show only the presence of a monomeric parent ion, but the solution aggregation may be different. The crossover experiment with **14** and **15** suggests the arenethiolate groups exchange on a chemical time scale since three distinct species (eq 1) are observed by DEPT135 NMR spectroscopy (Figure 2). Compounds **14** and **15** were identified by their chemical shifts in the DEPT NMR spectrum, and resonances lying near (or between) those for **14** and **15** are assigned to CymOs(SXyl)(SMes).

The variable temperature ^1H NMR spectra of **14** and **15** (Figure 1) each showed two compounds at lower temperatures. This suggests that several equilibrium or exchange processes were slowed as the temperature was decreased. An explanation consistent with the data is the formation of dimers at low temperature in solution. These dimers can undergo bridge–terminal exchange and cis–trans isomerization (Scheme 8). At room temperature, $[CymOs(SAr)_2]_2$ dissociation to monomers would account for crossover reactions resulting in the formation of CymOs(SXyl)(SMes) or CymOs(SXyl)(S-*t*-Bu) (eq 1). This is slowed at −21 °C and two complexes (trans and cis) are observed in a 2:1 ratio. Further cooling slows the rate of bridge–terminal exchange, in which an Os–S bond of a bridging arenethiolate (SAr_B) is first broken. The major isomer undergoes slower bridge–terminal exchange than the minor analog, on the basis of the −60 °C ^1H NMR spectrum of **14** (Figure 1f) and the −65 °C spectrum of **15** ($\Delta G^{\ddagger}_A$(exchange) > $G^{\ddagger}_B$(exchange)). The ^1H NMR integrations of the spectra of both **14** and **15** at these temperatures suggest that the species that undergoes slower bridge–terminal exchange is the more populous. Complete dissociation to monomers is an alternate route for cis–trans isomerization, but it does not help to reconcile the different rates of bridge–terminal exchange.

The results of the variable temperature experiments suggest that the nuclearity of the thiolate complexes is governed by the size of the substituent. The smaller S-*p*-tol compound (**16**) appears to be a dimer and the large S-*t*-Bu ligand of **13** enforces a monomeric structure, but can form a mixed bridging complex with **14**, as postulated in the crossover experiment. We are currently not able to confidently assign structures for the SXyl (**14**) and SMes (**15**) complexes but both monomeric and dimeric forms are presumably accessible.

Scheme 8

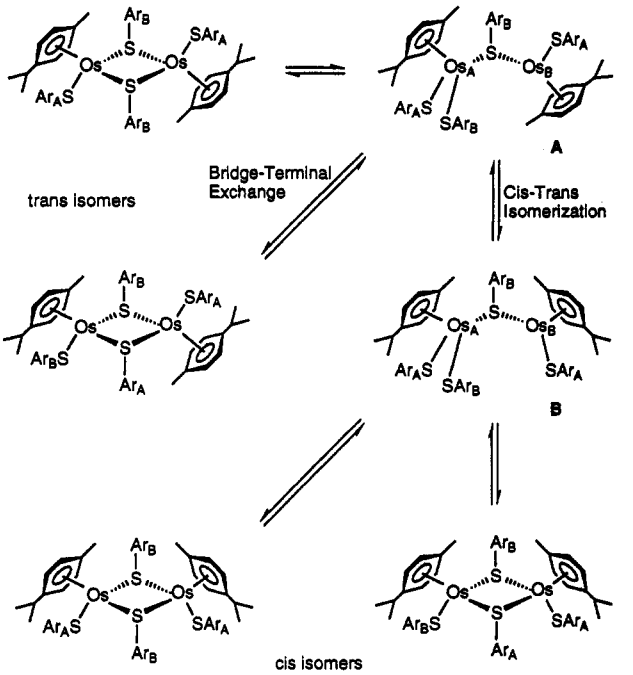

Table 4. pK_a Data for Several Carbon Acid Compounds

carbon acid	pK_a (DMSO)[28]
$H_2C(COMe)_2$	13.3
$H_2C(COPh)_2$	13.4
$H_2C(CO_2Me)_2$	16.4
PhCOMe	24.7

Synthesis of Carbon Acid Complexes. Imide **2** also reacts with carbon acids, and the pK_a values for several of these acids are shown in Table 4. These values coincide with the reactivity trends toward imide **2**, such that the

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(35) For a review of transition metal-mediated carbonyl coupling reactions including pinacolate complexes, see: Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733.
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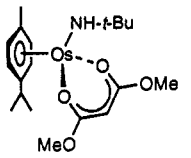


Figure 4. Alternative structure for 17.

more acidic C–H bond of $H_2C(COMe)_2$ added two diketones with *tert*-butylamine loss to give 18, the weaker acid ($H_2C(CO_2Me)_2$) adds across the Os–N bond to give 17, and the less acidic C–H bond of PhCOMe does not react with 2. This trend also applies to the reactivity of 17 with $H_2C(COR)_2$ (R = Me, Ph), which yields 22 and 23, and $H_2C(CO_2Me)_2$, which shows no reactivity.

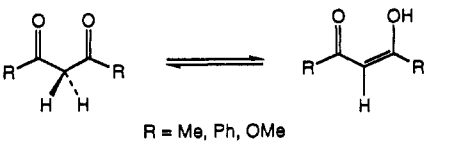
The ability of a proton donor to precoordinate to the metal center (or chelate) must play a role in these σ-ligand metathesis reactions. This is particularly apparent when comparing PhCOMe to the heteroatom reagents (Table 3). Although PhCOMe, with a pK_a of 24.7 (in DMSO), did not react with imido complex 2, $XylNH_2$, with a pK_a of 32.2, reacted to form xylylimide CymOsNXyl (25).[11,14] The mechanism proposed for the imide/amine exchange involves precoordination of the reacting amine.[11] Any mechanism involving hydrogen bonding alters the simple pK_a argument.

Solution Structure of Diketonate Complexes. Some structural questions arise in viewing these carbon acid compounds, and NMR spectroscopy was important in determining the structure of amide–malonate complex 17. The NH and CH resonances in the ^{1}H NMR spectrum were assigned by comparison with the spectrum of the deuterated compound 17-d_2. This confirmed the existence of the late metal–alkylamide bond, of which there are few examples.[1,2] The commonly observed β-elimination pathway[25,26,40] is not available here, helping to stabilize the NH-*t*-Bu fragment.

The most striking feature of complex 17, however, is that the diester ligand appears (on the basis of the J_{CH} value of 138 Hz) to adopt a conformation that leaves the osmium center formally unsaturated, rather than adopting the 18-electron O,O-bound malonate bonding mode shown in Figure 4, or some O,C-hybrid bonding.[41] The nuclear spin of ^{187}Os ($I = {}^1/_2$) offered the opportunity to verify the proposed connectivity by observing the $^1J(^{187}Os—^{13}C)$ and $^2J(^{187}Os—^1H)$ couplings. The $^{13}C\{^1H\}$ NMR spectrum of 17 (Figure 3) showed several satellites, due to both ^{187}Os—^{13}C coupling and the ^{13}C—^{13}C couplings. The nearly equal natural abundance of the two nuclei (^{13}C (1.1%) and ^{187}Os (1.64%)) made unequivocal assignment of coupling constants difficult in the 1D experiment. A 2D inverse ^{1}H–^{13}C correlation (HMQC)[20] performed with ^{13}C decoupling during acquisition (Figure 3) established $^1J_{OsC}$ = 56.6 Hz and $^2J_{OsH}$ = 10.8 Hz by observation of the satellites due to the ^{187}Os—^{13}C—^{1}H isotopomer (0.018% abundant). The second set of satellites is due to the ^{1}H—^{13}C—^{13}C=O isotopomer (0.024% abundant). This is further confirmed by performing the experiment without ^{13}C decoupling, in which case an extra splitting due to $^3J_{^1H—^{13}C=O}$ (=4 Hz) is introduced in the satellites of the ^{1}H—^{13}C—^{13}C=O isotopomer. Although there is some information in the literature on $J(^{187}Os—X)$ (X = H, P),[42,43] coupling constant data for ^{187}Os—^{13}C are rare, appearing only for carbonyl clusters,[44,45] on samples that were enriched with either ^{187}Os or ^{13}C. $^2J_{OsH}$ values have been reported for some osmium methyl complexes[46] where the values were considerably smaller than in this case (5.4–6.0 Hz). The 2D technique used here can be performed at natural abundance and generated the coupling information in a short period of time (ca. 4 h). The observation of the $^2J_{OsH}$ coupling also facilitated the observation of the ^{187}Os resonance of 17 (δ_{Os} = −1155) *via* a 2D ^{1}H—^{187}Os HMQC experiment, further confirming the binding mode of this ligand. A similar experiment was performed on CymOs[CH(COMe)$_2$-*C*][(OC(Me))$_2$CH-*O,O*] (18) which revealed δ^{187}Os = −628 and $^2J_{OsH}$ = 7.9 Hz for the proton of the C-bound acac ligand.

The mono-β-diketonato complexes 19–21 showed a J_{CH} value of 158–160 Hz (Table 2), which is consistent with the presence of sp^2 carbon centers and O,O-binding in the diketonate ligands.[41] These values were useful in making proper NMR assignments for bis(acetylacetonato) complex 18. Other (mono)acetylacetonato complexes of Cp*Ir[47] and CymRu[48] gave informative chemical shift and coupling data as well. They do not show infrared absorption bands above 1625 cm^{-1} for the C–O bonds, which is also true for 19–21 (not including the carbonyl absorptions of OAc). Cp*Ir(acac-*C*)(acac-*O,O*) has been prepared from [Cp*IrCl$_2$]$_2$, Na_2CO_3, and acacH,[47] but the reaction of [CymOsCl$_2$]$_2$, K_2CO_3, and acacH gave only (mono)diketonato complex 19. This complex, as well as the $(PhCO)_2CH$ derivative 20, are spectroscopically similar to those in the Ir and Ru systems (Table 2).

Various palladium diketonato complexes have been studied in an effort to determine what controls the linkage mode of the ligand.[49] The keto–enol character of the diketone was cited as the major factor governing the bonding type (O,O or C). This theory was further expanded in a review on this subject.[41] As applied to the osmium complexes, the keto–enol equilibrium correlates with the bonding observed in 17–23. The equilibrium of the free ligand (eq 7) parallels the preferred linkage mode



R = Me, Ph, OMe (7)

in the metal complexes. Consistent with the pK_a values (Table 4), the equilibrium lies much farther to the right for R = Me or Ph than for OMe.

Mechanism of Formation of 18. In the reaction of acacH with 2, the first step may be similar to those

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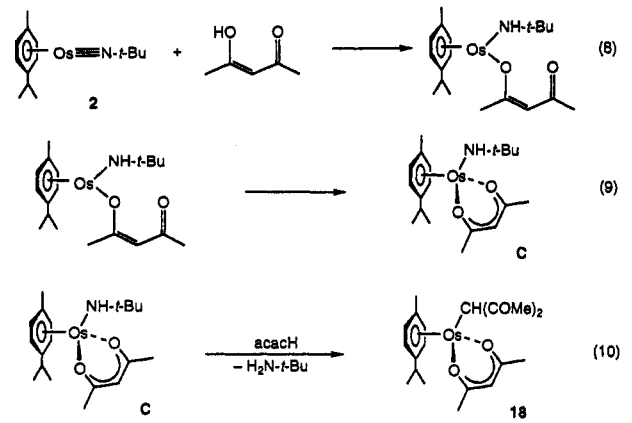
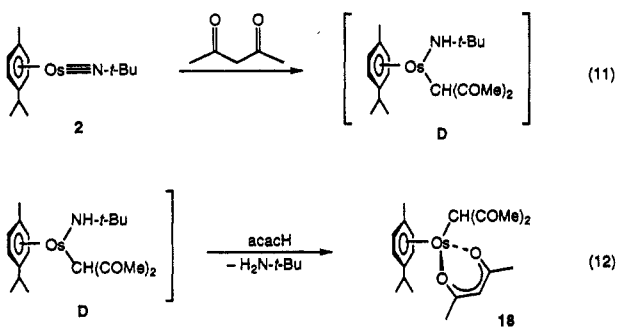
(48) Carmona, D.; Ferrer, J.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Elguero, J.; Jimeno, M. L. *J. Chem. Soc., Dalton Trans.* **1990**, 1463.
(49) Dash, G. C.; Mishra, R. C.; Panda, D.; Mohapatra, B. K. *Polyhedron* **1985**, *4*, 1297.

postulated for the reaction of **2** with alcohols (eq 8). The ketone oxygen can then donate electrons to the metal



center, generating a complex **C** (eq 9), which is structurally similar to **19–21**. Attack of **C** by another acacH could then lead to the observed product **18** and *tert*-butylamine (eq 10). Efforts to prepare intermediate **C** with **19** and LiNH-*t*-Bu were not successful, however, possibly due to the excess of LiNH-*t*-Bu. Li(acac) was presumably formed from the excess LiNH-*t*-Bu, preventing acacH from reacting with the **2** in solution.

Another possible intermediate is the C-bound complex **D** in eqs 11 and 12. If **17** can be considered a model for **D**, the addition of $H_2C(COR)_2$ (R = Me, Ph) to **17** to give



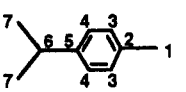
22 and **23** (Scheme 7) supports the intermediacy of **D** in the formation of **18**. Both **C** and **D** are plausible, and rearrangement at the metal center due to other known binding modes of β-diketones[41] may be reasonable in these intermediates, although ligand switching was not observed for Cp*Ir(acac)$_2$.[47] Regardless, the balance between C- or O,O-bound complexes, and mono- or disubstituted carbon acid complexes, is complicated.

Reactions of Carbon Acid Complexes. The reactivity of complexes **17–23** is also intricate. The 16-electron species **17** does not add donor ligands. However, changing N-*t*-Bu for NXyl by treatment of **17** with H_2NXyl appears to proceed through CymOs(NHXyl)[CH(CO$_2$Me)$_2$] but continues on to xylylimide **25** (Scheme 5), further demonstrating how delicate the balance is in these ligand arrangements. Of note is the fact that while **17** is formed from **2** and dimethyl malonate, a second equiv of $H_2C(CO_2Me)_2$ will not displace H_2N-*t*-Bu from **17** to give CymOs[(OC(OMe))$_2$CH-*O,O*][CH(CO$_2$Me)$_2$-*C*]. The β-diketones $H_2C(COR)_2$ (R = Me, Ph), though, readily protonate the NH-*t*-Bu ligand of **17** to give **22** and **23**. This again correlates with the pK_a values (Table 4), such that only the more acidic diketones will react with **17**.

Attempts to replace the Cl or OAc ligands of **19** or **21** with diketonates did not lead to (bis)diketonato complexes (i.e. **18**), and **19** did not give CymOs(acac)(O-*t*-Bu) with KO-*t*-Bu. In contrast, CymRu(acac)Cl reacts smoothly with X$^-$ to give CymRu(acac)X (X = halogens, azide, pyrazole and its derivatives).[48] This difference in reactivity is presumably due to the change from the second- to the third-row transition metals.[50] Despite the difficulties encountered in reactions with M(diketonate), **18** was easily prepared from imide **2** and 2 equiv of acacH.

Experimental Section

General Data. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a Vacuum Atmospheres 553-2 drybox equipped with a MO-40-2 inert gas purifier, or using standard Schlenk techniques. The amount of O_2 in the drybox atmosphere was monitored by a Teledyne Model No. 316 trace oxygen analyzer. All ^{1}H NMR spectra were recorded on either a 200-MHz or a 300-MHz Fourier transform instrument constructed at the University of California, Berkeley, NMR facility by Mr. Rudi Nunlist (equipped with Nicolet model 1280 data collection systems), or a Bruker AM-400, AM-500, and AMX-400 spectrometers. For ^{13}C{^{1}H} NMR chemical shift assignments, the *p*-cymene carbon atoms are numbered as follows:[51]



The 2D ^{1}H–^{13}C spectra were recorded on a Bruker AMX-300 spectrometer at 27 °C using the standard HMQC technique,[20,52] including a BIRD pulse and an optimized delay for suppression of ^{12}C bound proton signals, spectra being recorded both with and without ^{13}C decoupling. 2D ^{1}H–^{187}Os HMQC spectra[52] were recorded on a Bruker AMX 600 spectrometer at 25 °C operating at 600.14 and 13.68 MHz for ^{1}H and ^{187}Os, respectively. A broad-band VSP probe was used on which the 90° pulse for ^{187}Os was ca. 40 μs. Initially, a wide sweep width (5200 ppm) was used in the ^{187}Os dimension (f_1) to locate ^{187}Os resonances. The experiment was then run with a narrower sweep width (731 ppm) to improve digital resolution and rule out folding of the ^{187}Os resonance. Delays in the HMQC experiments were optimized for the appropriate value of $^2J(^{187}Os–^1H)$. ^{187}Os chemical shifts were set relative to OsO_4 by using I(OsO_4) = 2.282 343 with downfield shifts being positive.

Infrared spectra were recorded on a Nicolet 510 Fourier transform spectrometer or a Mattson Galaxy Series FTIR 3000 spectrometer. Elemental analyses were conducted by the University of California, Berkeley, Microanalysis Facility, and mass spectra were recorded by the University of California, Berkeley, Mass Spectrometry laboratory on AEI MS-12 or Kratos MS-50 mass spectrometers. Mass spectral results are reported by the most abundant isotopes (i.e. ^{192}Os). When transferring condensable gases, neat gas was allowed to expand into a bulb of known volume at a known temperature and then it was condensed into the reaction flask at –196 °C. The pressure of the added gas was measured with a MKS Baratron gauge.

Benzene, tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium–benzophenone. Pentane and hexane were distilled from lithium aluminum hydride. Methylene chloride was distilled from CaH_2 and acetone was distilled from $MgSO_4$. [CymOsCl$_2$]$_2$[53] (Cym = η^6-*p*-Cymene) (1) and CymOsN-

(50) Ziegler, T.; Cheng, W.; Baerends, E. J.; Ravenek, W. *Inorg. Chem.* **1988**, *27*, 3458.
(51) Arthur, T.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 369.
(52) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.
(53) Kiel, W. A.; Ball, R. G.; Graham, W. A. G. *J. Organomet. Chem.* **1990**, *383*, 481.

t-Bu[11,14] were prepared by literature methods. Amines H_2N-*t*-Bu and $H_2N(2,6\text{-}Me_2C_6H_3)$ were stirred over CaH_2 for 24 h and then distilled under reduced pressure before use. All $1,2\text{-}(HX)_2C_6H_3$ (X = O, NH) and H_2N-*p*-tol were purified by sublimation. Thiols HSR (R = *t*-Bu, Xyl) were dried over CaH_2 then distilled under reduced pressure before use. Trimethylphosphine was purchased from the Strem Chemical Co. and vacuum transferred from Na/K. Unless otherwise noted, all other reagents were used as received from commercial suppliers.

CymOs(O-*t*-Bu)$_2$ (3). A solution of KO-*t*-Bu (45 mg, 0.40 mmol) in THF (3 mL) was added dropwise to a stirred solution of **1** (104 mg, 0.132 mmol) in THF (8 mL). The solvent was removed under reduced pressure after 5 min. The residue was dissolved in pentane (5 mL) and filtered. The solvent was removed from the filtrate *in vacuo* giving 44 mg (0.94 mmol, 47%) of deep-red **3** as an oily solid: ^{1}H NMR (C_6D_6) δ 5.81 (d, J = 5.9 Hz, 2H, $MeC_6H_4CHMe_2$), 5.75 (d, J = 6.0, 2H, $MeC_6H_4CHMe_2$), 2.24 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.81 (s, 3H, $MeC_6H_4CHMe_2$), 1.53 (s, 18H, $C(CH_3)_3$), 1.20 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 83.8 (C5), 78.3 ($C(CH_3)_3$), 73.9 (C2), 70.2 (C3 or C4), 68.3 (C3 or C4), 33.7 ($C(CH_3)_3$), 33.5 (C6), 23.6 (C7), 21.7 (C1); IR (KBr) 2961 (s), 2925 (m), 2870 (m), 1467 (w), 1383 (w), 1363 (w), 1019 (w), 869 (w), 839 (w), 816 (w). The thermal instability of **3** precluded microanalysis.

Reaction of 3 with H_2N-*t*-Bu. CymOs(O-*t*-Bu)$_2$ (**3**) (10 mg, 0.021 mmol) was dissolved in C_6D_6 (0.7 mL). The solution was degassed using a freeze–pump–thaw cycle, and H_2N-*t*-Bu (0.021 mmol) was added by vacuum transfer. The ^{1}H NMR spectrum of this solution showed resonances for complex **2** in 80% yield (verified by comparison with an authentic sample) and HO-*t*-Bu.

CymOs(NH-*t*-Bu)[OCMe(CF$_3$)$_2$] (4). A stirred toluene solution (7 mL) of **2** (47.3 mg, 0.120 mmol) was treated with $HOCMe(CF_3)_2$ (53 mg, 0.29 mmol) in toluene (2 mL). The solution was stirred for 10 min, and the solvent was then removed *in vacuo*. The solid residue was extracted into $(Me_3Si)_2O$, filtered through Celite, and the solvent was removed from the filtrate under reduced pressure leaving 59.9 mg (0.104 mmol, 87%) of a red-orange thick oil **4**: ^{1}H NMR (C_6D_6) δ 11.07 (br s, 1H, NH), 5.34 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 5.24 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 2.15 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.89 (s, 3H, $MeC_6H_4CHMe_2$), 1.44 (s, 3H, $OCMe(CF_3)_2$), 1.13 (s, 9H, CMe_3), 1.11 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 125.9 (quart, J = 291.7, $OCMe(CF_3)_2$), 86.7 (C5), 80.3 (sept, J = 27.0, $OCMe(CF_3)_2$), 77.4 (C2), 70.3 (br s, C3 or C4), 69.2 (br s, C3 or C4), 61.0 (CMe_3), 32.8 (C6), 32.1 (CMe_3), 24.1 (C7), 22.0 ($OCMe(CF_3)_2$), 21.3 (C1); $^{19}F\{^1H\}$ NMR (C_6D_6) δ −77.8; IR (CH_2Cl_2) 3061 (w), 2997 (w), 2966 (m), 1475 (m), 1385 (m), 1365 (m), 1358 (m), 1306 (m), 1207 (s), 1182 (s), 951 (m), 870 (m), 1103 (s), 1032 (m), 1078 (s) cm^{-1}. The compound is an uncrystallizable oil, and attempts at microanalysis were unsuccessful.

CymOs[OC(CH$_3$)$_2$C(CH$_3$)$_2$O] (5). $HOC(CH_3)_2C(CH_3)_2OH$ (32 mg, 0.27 mmol) in pentane (3 mL) was added dropwise to a pentane solution (10 mL) of **2** (76 mg, 0.19 mmol) with stirring. The solution was stirred at room temperature for 1 h and the solvent was then removed under reduced pressure giving an oil. Crystallization of the oil from Et_2O at −30 °C gave red needles of **5** (29 mg, 0.066 mmol) in 34% yield. An independent experiment on a small scale in C_6D_6 showed that **5** was generated in solution in >98% NMR yield: ^{1}H NMR (C_6D_6) δ 5.82 (d, J = 6.0, 2H, $MeC_6H_4CHMe_2$), 5.73 (d, J = 5.9, 2H, $MeC_6H_4CHMe_2$), 2.28 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.95 (s, 3H, $MeC_6H_4CHMe_2$), 1.39 (s, 12H, $OCMe_2CMe_2O$), 1.20 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 88.3 (C5), 85.6 ($OCMe_2CMe_2O$), 78.3 (C2), 68.8 (C3 or C4), 66.3 (C3 or C4), 33.7 (C6), 27.5 ($OCMe_2CMe_2O$), 23.4 (C7), 21.0 (C1); electron impact mass spectrum (EIMS) parent ion envelope *m/e* (obs *I*, calc *I*) 439 (45.8, 44.6), 440 (89.7, 71.1), 442 ([M]$^+$, 100, 100); IR (KBr) 3035 (m), 2963 (s), 2924 (m), 1443 (w), 1379 (w), 1353 (w), 1134 (s), 948 (m), 893 (m), 719 (w), 649 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_2Os$: C, 43.62; H, 5.95. Found: C, 43.66; H, 5.68.

CymOs[1,2-O$_2$C$_6$H$_4$] (6). A toluene solution (2 mL) of $1,2\text{-}(HO)_2C_6H_4$ (15 mg, 0.14 mmol) was added to a stirred toluene solution (3 mL) of **2** (51 mg, 0.13 mmol). The color of the solution immediately changed to red. The solvent was removed *in vacuo* after 20 min. The residue was washed with pentane (1 mL), extracted into Et_2O, and filtered through Celite. The filtrate was concentrated to 3 mL, layered with 1 mL of pentane, and cooled to −40 °C. After 12 h a red precipitate was collected, yielding 39 mg of product (0.090 mmol, 69%): ^{1}H NMR (C_6D_6) δ 7.69 (dd, J_1(apparent) = 5.9, J_2(apparent) = 3.5, 2H, C_6H_4), 6.9 (dd, J_1(apparent) = 5.9, J_2(apparent) = 3.4, 2H, C_6H_4), 5.85 (d, J = 5.8, 2H, $MeC_6H_4CHMe_2$), 5.73 (d, J = 5.8, 2H, $MeC_6H_4CHMe_2$), 2.17 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.82 (s, 3H, $MeC_6H_4CHMe_2$), 1.08 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 165.6 (*ipso*-C_6H_4), 119.7 (C_6H_4), 115.2 (C_6H_4), 90.3 (C5), 80.9 (C2), 68.0 (C3 or C4), 65.6 (C3 or C4), 33.3 (C6), 23.2 (C7), 20.5 (C1); IR (KBr) 3057 (m), 3045 (m), 2964 (m), 2920 (m), 2870 (w), 2900 (w), 1471 (s), 1259 (s), 814 (m), 806 (m), 754 (m), 661 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2Os$: C, 44.43; H, 4.19. Found: C, 44.40; H, 4.13.

Generation of 6 in Solution from 5. An NMR tube was charged with **5** (5.5 mg, 0.012 mmol), Cp_2Fe (1.3 mg, 0.0070 mmol, 0.58 equiv), and C_6D_6 (0.7 mL). Two one pulse ^{1}H NMR spectra were acquired. The ring bound methyl resonances of the *p*-cymene were integrated vs the Cp resonances of the internal standard, and the values from the two spectra were averaged. Under an atmosphere of N_2, catechol (1.6 mg, 0.015 mmol, 1.3 equiv) was added at 25 °C. ^{1}H NMR spectra were obtained after 8 h, as described above. In this manner the yield was determined to be 59%. The NMR spectra from this reaction were identical to those of **6** prepared from **2**. No resonances for the osmium starting material were observed.

CymOs[1,2-O(NH)C$_6$H$_4$] (7). A toluene solution (3 mL) of $1,2\text{-}(HO)(H_2N)C_6H_4$ (20 mg, 0.18 mmol) was added to a stirred toluene solution (3 mL) of **2** (72 mg, 0.18 mmol). The color of the solution changed to deep red, and the solvent was removed *in vacuo* after 30 min. The residue was washed with hexane (2 mL), extracted into toluene, and filtered. The solvent was removed from the filtrate under reduced pressure, yielding 78 mg of the deep-red solid product (0.18 mmol, 99%): ^{1}H NMR (C_6D_6) δ 8.68 (br s, 1H, NH), 7.64 (d, J = 7.8, 1H, C_6H_4), 7.22 (d, J = 7.7, 1H, C_6H_4), 7.02 (overlapping dd, J(apparent) = 7.2, 1H, C_6H_4), 6.88 (overlapping dd, J(apparent) = 7.3, 1H, C_6H_4), 5.46 (d, J = 4.7, 2H, $MeC_6H_4CHMe_2$), 5.39 (d, J = 4.8, 2H, $MeC_6H_4CHMe_2$), 2.17 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.91 (s, 3H, $MeC_6H_4CHMe_2$), 1.07 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 167.5 (O-*ipso*-C_6H_4), 151.7 (N-*ipso*-C_6H_4), 119.9 (C_6H_4), 118.0 (C_6H_4), 115.2 (C_6H_4), 114.2 (C_6H_4), 90.8 (C5), 80.5 (C2), 68.4 (C3 or C4), 66.0 (C3 or C4), 33.0 (C6), 23.9 (C7), 20.8 (C1); IR (KBr) 3342 (m), 3066 (m), 3049 (m), 2956 (m), 2926 (s), 2868 (m), 1579 (m), 1479 (s), 1450 (m), 1298 (s), 1273 (s), 1246 (m), 811 (m), 714 (m), 737 (s), 702 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{19}NOOs$: C, 44.53; H, 4.44; N, 3.25. Found: C, 44.27; H, 4.42; N, 3.33.

CymOs[1,2-O$_2$C$_6$H$_4$](PMe$_3$) (8). A C_6D_6 solution (0.7 mL) of **6** (6.0 mg, 0.014 mmol) was degassed using one freeze–pump–thaw cycle. Neat PMe_3 (0.014 mmol) was condensed into the reaction flask at −196 °C, and the flask was then allowed to warm to room temperature and stir for 1.5 h. The solvent was removed *in vacuo* and the orange residue was washed with pentane (1 mL), extracted into toluene, and filtered through Celite. The solvent was removed from the filtrate under reduced pressure, yielding 7.0 mg, of product (0.14 mmol, 99%): ^{1}H NMR (C_6D_6) δ 7.19 (dd, J_1(apparent) = 5.7, J_2(apparent) = 3.5, 2H, C_6H_4), 6.76 (dd, J_1(apparent) = 5.7, J_2(apparent) = 3.5, 2H, C_6H_4), 4.90 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 4.70 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 2.40 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.92 (s, 3H, $MeC_6H_4CHMe_2$), 1.07 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$), 0.89 (d, J_{HP} = 10.3, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 165.8 (*ipso*-C_6H_4), 116.3 (C_6H_4), 114.0 (C_6H_4), 78.2 (J_{CP} = 5.3, C3 or C4), 77.5 (J_{CP} = 5.3, C3 or C4), 31.6 (C6), 23.1 (C7), 17.8 (C1), 13.8 (J_{CP} = 32.8, PMe_3) (resonances for C5 and C2 were not observed at room

temperature); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −23.3. Satisfactory microanalytical data were not obtained after several attempts.

Reaction of 6 with 1,2-$(H_2N)_2C_6H_4$. An NMR tube was charged with **6** (4.4 mg, 0.010 mmol), Cp_2Fe (1.4 mg, 0.0075 mmol, 0.7 equiv), and C_6D_6 (0.7 mL). Two one pulse ^1H NMR spectra were acquired. The ring bound methyl resonances of the *p*-cymene were integrated vs the Cp resonances of the internal standard, and the values from the two spectra were averaged. Under an atmosphere of N_2, 1,2-$(H_2N)_2C_6H_4$ (1.4 mg, 0.013 mmol, 1.3 equiv) was added at 25 °C. The solution was subjected to a freeze–pump–thaw cycle. The ^1H NMR spectrum at this time showed a new compound **9**. The solution was heated at 45 °C for 19 h, giving CymOs[$(NH)_2C_6H_4$] (**10**),[11] and ^1H NMR spectra were obtained as described above. In this manner the yield was determined to be 98%. ^1H NMR data for **9** (C_6D_6): δ 7.31 (m, 2H, C_6H_4), 6.85 (m, 2H, C_6H_4), 5.01 (d, J = 5.3, 2H, $MeC_6H_4CHMe_2$), 4.76 (d, J = 5.3, 2H, $MeC_6H_4CHMe_2$), 2.32 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.76 (s, 3H, $MeC_6H_4CHMe_2$), 1.05 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$).

Generation of (1,2-Diamidobenzene)osmium/Catechol Complex 11. A C_6D_6 (0.5 mL) solution containing 5.6 mg of **10** (0.013 mmol) and 4.0 mg of catechol (0.036 mmol) was prepared. The resulting solution indicated the presence of starting materials plus the new hydrogen-bonded complex. ^1H NMR data for **11** (C_6D_6): δ 7.26 (m, 2H, C_6H_4), 6.25 (m, 2H, C_6H_4), 5.21 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 4.99 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 2.26 (sept, J = 6.5, 1H, $MeC_6H_4CHMe_2$), 1.49 (s, 3H, $MeC_6H_4CHMe_2$), 0.91 (d, J = 6.5, 6H, $MeC_6H_4CHMe_2$).

Generation of the Osmium Catecholate/*p*-Toluidine Complex 12. A C_6D_6 (0.5 mL) solution containing 3.0 mg of **6** (0.0047 mmol) and 1.0 mg of *p*-toluidine (0.0092 mmol) was prepared and subjected to NMR analysis, which demonstrated the presence of the adduct **12**, and analyzed by ^1H NMR spectrometry. After analysis, the solvent was lyophilized under vacuum and the reaction mixture was redissolved in C_6D_6. The spectrum of this sample remained unchanged, except that excess *p*-toluidine had been removed. ^1H NMR data for **12** (C_6D_6): δ 7.64 (m, 2H, C_6H_4), 6.90 (m, 2H, C_6H_4), 6.84 (d, J = 6.5, 2H, $NH_2C_6H_4Me$), 6.34 (d, J = 6.5, 2H, $NH_2C_6H_4Me$), 5.64 (d, J = 4.4, 2H, $MeC_6H_4CHMe_2$), 5.40 (d, J = 4.4, 2H, $MeC_6H_4CHMe_2$), 2.19 (sept, J = 5.5, 1H, $MeC_6H_4CHMe_2$), 2.10 (s, 3H, $NH_2C_6H_4Me$), 1.83 (s, 3H, $MeC_6H_4CHMe_2$), 1.09 (d, J = 5.5, 6H, $MeC_6H_4CHMe_2$).

CymOs(S-*t*-Bu)$_2$ (13). A solution of **2** (34 mg, 0.084 mmol) in toluene (5 mL) was degassed using a freeze–pump–thaw cycle and HS-*t*-Bu (0.18 mmol) was condensed onto the solution at −196 °C. The solid was warmed to room temperature and stirred for 40 min. Solvent was removed *in vacuo*, the residual solid was extracted with pentane (3 mL), and the solution was filtered. The solvent was removed from the filtrate under reduced pressure leaving purple solid **13** (40 mg, 0.080 mmol, 95%): ^1H NMR (C_6D_6) δ 5.62 (d, J = 5.9, 2H, $MeC_6H_4CHMe_2$), 5.55 (d, J = 5.5, 2H, $MeC_6H_4CHMe_2$), 2.19 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.83 (s, 3H, $MeC_6H_4CHMe_2$), 1.71 (s, 18H, $C(CH_3)_3$), 1.13 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 89.7 (C5), 79.9 (C2), 75.7 (C3 or C4), 73.7 (C3 or C4), 50.6 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 32.7 (C6), 24.1 (C7), 21.3 (C1); EIMS parent ion envelope *m/e* (obs *I*, calc *I*) 500 (25.4, 31.2), 501 (41.3, 43.3), 502 (73.0, 70.9), 503 (14.3, 17.6), 504 ([M]$^+$, 100, 100), 505 (14.3, 21.4); IR (KBr) 2963 (s), 2928 (s), 2911 (s), 1445 (m), 1355 (m), 1149 (s), 867 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{32}OsS_2$: C, 43.00; H, 6.42. Found: C, 43.32; H, 6.38.

Generation of 13 in Solution from 3. A solution of **3** (6 mg, 0.01 mmol) in C_6D_6 (0.7 mL) was degassed using one freeze–pump–thaw cycle and *t*-BuSH (0.033 mmol) was added by vacuum transfer at −196 °C. The color changed immediately from deep red to violet. An ^1H NMR spectrum of this solution showed resonances for complex **13** in 92% yield (verified by comparison with a sample from the preparative scale reaction carried out above) and HO-*t*-Bu in 100% yield.

CymOs(S-2,6-Me$_2$C$_6$H$_3$)$_2$ (14). A solution of **2** (26 mg, 0.066 mmol) in toluene (5 mL) was treated with HS-2,6-$Me_2C_6H_3$ (18 mg, 0.13 mmol) in toluene (2 mL). The solution immediately became purple, and it was stirred for 15 min before the solvent was removed *in vacuo*. The solid residue was washed with 15 mL of pentane, extracted into Et_2O (15 mL), and the solution was filtered through Celite. The solvent was removed from the filtrate leaving purple solid **14** (33 mg, 0.055 mmol, 83%): ^1H NMR (C_6D_6) δ 7.12 (d, J = 6.7, 4H, *m*-C_6H_3), 6.98 (t, J = 7.7, 2H, *p*-C_6H_3), 5.05 (d, J = 5.1, 2H, $MeC_6H_4CHMe_2$), 4.78 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 2.56 (s, 12H, $Me_2C_6H_3$), 2.13 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.64 (s, 3H, $MeC_6H_4CHMe_2$), 1.09 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 139.7 (quat Xyl), 127.9 (*m*-Xyl), 126.1 (*p*-Xyl), 90.2 (C5), 80.2 (C2), 76.2 (C3 or C4), 73.6 (C3 or C4), 32.7 (C6), 23.5 (C7 or $Me_2C_6H_3$), 22.7 (C7 or $Me_2C_6H_3$), 20.0 (C1) (one of the quaternary carbon signals for the Xyl ligand was not observed at room temperature); IR (KBr) 3082 (w), 3051 (w), 2960 (s), 2937 (m), 2918 (m), 1581 (m), 1456 (s), 1433 (m), 1377 (w), 1047 (m), 1032 (m), 860 (m), 795 (w), 771 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{32}OsS_2$: C, 52.15; H, 5.39. Found: C, 52.33; H, 5.43.

CymOs(S-2,4,6-Me$_3$C$_6$H$_2$)$_2$ (15). This purple solid was prepared in 94% yield using HS-2,4,6-$Me_3C_6H_2$ (23 mg, 0.15 mmol) and **2** (27.4 mg, 0.069 mmol) by a method similar to that used to prepare **14**. ^1H NMR (C_6D_6) δ 6.95 (s, 4H, *m*-C_6H_2), 5.09 (br s, 2H, $MeC_6H_4CHMe_2$), 4.83 (br d, J = 5.1, 2H, $MeC_6H_4CHMe_2$), 2.55 (br s, 12H, *o*-$Me_3C_6H_2$), 2.23 (br s, 6H, *p*-$Me_3C_6H_2$), 2.17 (sept, J = 6.8, 1H, $MeC_6H_4CHMe_2$), 1.69 (s, 3H, $MeC_6H_4CHMe_2$), 1.13 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 34 °C) δ 135.0 (*p*-C_6H_2), 139.4 (quat-C_6H_2), 128.8 (*m*-C_6H_2), 90.2 (C5), 80.2 (C2), 76.3 (C3 or C4), 73.6 (C3 or C4), 32.8 (C6), 23.6 (C7), 22.6 (*o*-$Me_3C_6H_2$), 20.9 (*p*-$Me_3C_6H_2$), 20.1 (C1) (one of the quaternary carbon signals for the Xyl ligand was not observed at room temperature); IR (KBr) 3064 (w), 3010 (w), 2960 (s), 2947 (s), 2918 (s), 2871 (m), 1599 (m), 1458 (s), 1431 (s), 1375 (w), 1057 (m), 1030 (m), 862 (m), 850 (m), 793 (m) cm^{-1}. High resolution electron impact mass spectrum (HREIMS): calcd for $C_{28}H_{36}{}^{192}OsS_2$ (M$^+$), 628.187332; found, 628.187400. Anal. Calcd for $C_{28}H_{36}OsS_2$: C, 53.65; H, 5.79. Found: C, 53.50; H, 5.83.

Thiolate Crossover Reactions. Complexes **14** (5.4 mg, 0.0090 mmol) and **15** (4.6 mg, 0.0073 mmol) were mixed in C_6D_6 (0.7 mL). The $^{13}C\{^1H\}$ NMR and DEPT135 spectra at 40 °C are consistent with a statistical mixture (ca. 1:2:1) of **14**, CymOs(S-2,6-$Me_2C_6H_3$)(S-2,4,6-$Me_3C_6H_2$), and **15**. Assignments can be made from the DEPT135 spectrum: DEPT135 NMR (C_6D_6) δ 128.8 (*m*-$Me_2C_6H_3$ or *m*-$Me_3C_6H_2$), 127.8 (*m*-$Me_2C_6H_3$ or *m*-$Me_3C_6H_2$), 126.0 (*p*-$Me_2C_6H_3$), 76.2 (C3 or C4), 73.5 (C3 or C4), 32.7 (C6), 23.5 (C7), 22.6 (*o*-$Me_2C_6H_3$ or *o*-$Me_3C_6H_2$), 22.5 (*o*-$Me_2C_6H_3$ or *o*-$Me_3C_6H_2$), 20.9 (*p*-$Me_3C_6H_2$), 20.0 (C1). CymOs(S-2,6-$Me_2C_6H_3$)(S-*t*-Bu) was observed in the ^1H NMR spectrum when **13** and **15** were mixed in C_6D_6: ^1H NMR (C_6D_6) δ 7.15 (m, 2H, *m*-$Me_2C_6H_3$), 7.02 (t, J = 7.4, 1H, *p*-$Me_2C_6H_3$), 5.23 (d, J = 5.5, 2H, $MeC_6H_4CHMe_2$), 5.10 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 2.60 (s, 6H, $Me_2C_6H_3$), 2.12 (sept, J = 6.8, 1H, $MeC_6H_4CHMe_2$), 1.73 (s, 3H, $MeC_6H_4CHMe_2$), 1.63 (s, 9H, CMe_3), 1.09 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$).

[CymOs(S-*p*-tol)$_2$]$_2$ (16). A stirred toluene solution (7 mL) of **2** (30 mg, 0.075 mmol) was treated with HS-*p*-tol (20 mg, 0.16 mmol) in toluene (3 mL). The color changed from yellow to deep red over 15 min. The solvent was evaporated *in vacuo* after 30 min. The green solid residue was washed with pentane, and extracted into toluene. This solution was filtered and the solvent was removed from the filtrate under reduced pressure, leaving 31 mg of product (0.027 mmol, 72%): ^1H NMR (C_6D_6) δ 8.41 (d, J = 8.0, 4H, C_6H_4Me), 7.51 (d, J = 8.0, 4H, C_6H_4Me), 6.97 (d, J = 8.1, 4H, C_6H_4Me), 6.88 (d, J = 7.9, 4H, C_6H_4Me), 5.05 (d, J = 5.4, 4H, $MeC_6H_4CHMe_2$), 4.99 (d, J = 5.6, 4H, $MeC_6H_4CHMe_2$), 2.28 (sept, J = 6.9, 2H, $MeC_6H_4CHMe_2$), 2.15 (s, 6H, C_6H_4Me), 2.11 (s, 6H, C_6H_4Me), 1.91 (s, 6H, $MeC_6H_4CHMe_2$), 0.92 (d, J = 6.9, 12H, $MeC_6H_4CHMe_2$). The instability of **16** has prevented further characterization.

CymOs(NH-*t*-Bu)[CH(CO$_2$Me)$_2$] (17). A stirred toluene solution (4 mL) of **2** (66.7 mg, 0.169 mmol) was treated with 1 equiv of $H_2C(CO_2Me)_2$ (22.3 mg, 0.169 mmol) in toluene (4 mL). The solvent was evaporated *in vacuo* after the solution was stirred

for 47 h, leaving a dark red solid. The solid residue was extracted into pentane (10 mL) and filtered through Celite. The filtrate was concentrated to half volume and cooled to −40 °C. After 12 h a red solid had precipitated, and the solution was decanted, yielding 75.5 mg of product (0.143 mmol, 85%): ^{1}H NMR (C_6D_6) δ 13.20 (br s, 1H, NH), 5.47 (d, J = 5.8, 2H, $MeC_6H_4CHMe_2$), 5.44 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 4.83 (s, 1H, $CH(CO_2Me)_2$), 3.38 (s, 6H, $CH(CO_2Me)_2$), 2.17 (sept, J = 6.9, $MeC_6H_4CHMe_2$), 1.92 (s, 3H, $MeC_6H_4CHMe_2$), 1.23 (s, 9H, CMe_3), 1.07 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 174.4 ($CH(CO_2Me)_2$), 89.8 (C5), 77.6 (C2), 76.2 (C3 or C4), 73.6 (C3 or C4), 65.8 (CMe_3), 50.0 ($CH(CO_2Me)_2$), 36.7 (J_{CH} = 138, $^1J_{C-Os}$ (from the ^{1}H–^{13}C HMQC spectrum (Figure 3) = 56.6, $CH(CO_2Me)_2$), 32.5 (C6), 31.7 (CMe_3), 24.2 (C7), 21.4 (C1); ^{187}Os NMR (toluene-d_8) δ_{Os} = −1155 ($^2J_{OsH}$ = 10.6 Hz) from the ^{1}H–^{187}Os HMQC spectrum; IR (C_6H_6) 3261 (w), 2965 (m), 2945 (m), 2873 (w), 1731 (s), 1687 (m), 1432 (m), 1360 (m), 1252 (m), 1192 (m), 1112 (s), 1064 (m), 792 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{31}NO_4Os$: C, 43.25; H, 5.92; N, 2.65. Found: C, 42.93; H, 5.85; N, 2.61.

CymOs(ND-*t*-Bu)[CD(CO$_2$Me)$_2$] (17-*d*$_2$). The compound was prepared in 80% yield using LiNDPh by a method similar to that described above for the preparation of **17**. The ^{1}H NMR data were identical with those of **17**, except that no resonances were observed at δ 13.20 and 4.83. IR (C_6H_6): 2966 (m), 2945 (m), 2868 (w), 2425 (w), 1729 (s), 1687 (m), 1434 (m), 1363 (m), 1272 (s), 1188 (m), 1068 (s), 857 (m), 794 (m) cm^{-1}.

Reaction of 17 with H$_2$N(2,6-Me$_2$C$_6$H$_3$). A C_6D_6 solution (0.7 mL) of **17** (5.0 mg, 0.0095 mmol) was added to $H_2N(2,6\text{-}Me_2C_6H_3)$ (3.0 mg, 0.025 mmol). A ^{1}H NMR spectrum of the solution after 30 min showed >66% starting material, but also minor resonances (33%) consistent with CymOs[NH(2,6-$Me_2C_6H_3$)][$CH(CO_2Me)_2$]. The reaction did not progress further after 14 h. An additional 6 mg of amine was added to the solution, and the ^{1}H NMR spectrum at this time showed some CymOsN-(2,6-$Me_2C_6H_3$) (**25**), the sole organometallic product observed after 4 days. *tert*-Butylamine and $H_2C(CO_2Me)_2$ were present also. The solvent was lyophilized from the solution, and the residue was extracted into pentane and filtered through Celite. The solvent was removed from the filtrate under reduced pressure, leaving 3.5 mg (0.0079 mmol, 83%) of **25**.[14]

CymOs[CH(COMe)$_2$][(OC(Me))$_2$CH] (18). A stirred toluene solution (4 mL) of **2** (45.4 mg, 0.115 mmol) was treated with $H_2C(COMe)_2$ (24.7 mg, 0.247 mmol) in toluene (1 mL). The solution was stirred for 17 h, and the solvent was removed *in vacuo*. The solid residue was washed with pentane (1 mL) and extracted into Et_2O. The Et_2O solution was filtered through Celite, and the solvent was removed from the filtrate under reduced pressure, leaving 45 mg (0.085 mmol, 74%) of a yellow solid. A small amount of the solid was readily crystallized from pentane in 70% yield: ^{1}H NMR (C_6D_6) δ 5.39 (d, J = 5.5, 2H, $MeC_6H_4CHMe_2$), 5.26 (d, J = 5.4, 2H, $MeC_6H_4CHMe_2$), 5.12 (s, 1H, O,O-bound $(OC(Me))_2CH$), 4.61 (s, 1H, C-bound $CH(COMe)_2$), 2.38 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 2.02 (s, 6H, C-bound $CH(COMe)_2$), 1.69 (s, 6H, O,O-bound $(OC(Me))_2CH$), 1.67 (s, 3H, $MeC_6H_4CHMe_2$), 1.02 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 201.8 (C-bound $CH(COMe)_2$), 185.1 (O,O-bound $(OC(Me))_2CH$), 101.3 (J_{CH} = 159, O,O-bound $(OC(Me))_2CH$), 91.1 (C5), 82.3 (C2), 76.5 (C3 or C4), 73.1 (C3 or C4), 57.7 (J_{CH} = 134, C-bound $CH(COMe)_2$), 31.0 (C-bound $CH(COMe)_2$), 30.3 (C6), 27.3 (O,O-bound $(OC(Me))_2CH$), 22.5 (C7), 16.2 (C1); ^{187}Os NMR (toluene-d_8) δ_{Os} = −628 ($^2J_{OsH}$ = 7.9 Hz) from the ^{1}H–^{187}Os HMQC spectrum; IR (KBr) 3065 (m), 2966 (m), 2943 (m), 2924 (m), 2878 (w), 1678 (s), 1570 (s), 1528 (s), 1398 (m), 1378 (m), 1277 (m), 1183 (m), 1167 (m), 1037 (m), 881 (m), 656 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_4Os$: C, 45.96; H, 5.40. Found: C, 45.89; H, 5.51.

CymOs[(OC(Me))$_2$CH]Cl (19). A suspension of **1** (24 mg, 0.030 mmol) and K_2CO_3 (20.4 mg, 0.148 mmol) in acetone (2 mL) was stirred while $H_2C(COMe)_2$ (33 mg, 0.33 mmol) in acetone (1 mL) was added dropwise. The solution was stirred for 12 h, and the solvent was removed *in vacuo*. The yellow solid residue was extracted into Et_2O and filtered through Celite. The solvent was removed from the filtrate under reduced pressure leaving 28 mg (0.060 mmol, 100%) of a yellow solid. Crystallization from Et_2O gave **19** in 75% yield: ^{1}H NMR (C_6D_6) δ 5.53 (d, J = 5.4, 2H, $MeC_6H_4CHMe_2$), 5.21 (d, J = 5.3, 2H, $MeC_6H_4CHMe_2$), 5.14 (s, 1H, $(OC(Me))_2CH$), 2.58 (sept, J = 6.9, $MeC_6H_4CHMe_2$), 1.93 (s, 3H, $MeC_6H_4CHMe_2$), 1.76 (s, 6H, $(OC(Me))_2CH$), 1.11 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 186.0 ($(OC(Me))_2CH$), 100.7 (J_{CH} = 160, $(OC(Me))_2CH$), 89.1 (C5), 87.7 (C2), 73.8 (C3 or C4), 69.2 (C3 or C4), 31.6 (C6), 27.1 ($(OC(Me))_2CH$), 22.7 (C7), 17.9 (C1); IR (KBr) 3083 (w), 3060 (w), 3048 (m), 2961 (m), 2923 (m), 2870 (w), 1577 (s), 1561 (s), 1542 (m), 1432 (m), 1379 (s), 1276 (m), 1025 (m), 778 (m), 603 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{21}ClO_2Os$: C, 39.25; H, 4.61. Found: C, 38.90; H, 4.43.

Reaction of 19 with LiNH-*t*-Bu. A stirred solution of **19** (5 mg, 0.01 mmol) in THF (3 mL) was treated with a THF solution (2 mL) of LiNH-*t*-Bu (5 mg, 0.06 mmol). The solvent was removed *in vacuo* after 20 min, and the solid residue was extracted into pentane and filtered through Celite. The solvent was removed from the filtrate under reduced pressure, leaving 3.5 mg of **2** (0.0090 mmol, 90%).

CymOs[(OC(Ph))$_2$CH]Cl (20). To a stirred suspension of **1** (201 mg, 0.254 mmol) and K_2CO_3 (24.5 mg, 1.77 mmol) in acetone (10 mL) was added dropwise $H_2C(COPh)_2$ (130 mg, 0.580 mmol) in acetone (5 mL). The solution was stirred for 12 h, and the solvent was then removed *in vacuo*. The red solid residue was washed with pentane, extracted into THF, and filtered through Celite. The filtrate was concentrated to 1 mL and then cooled to −40 °C. A red precipitate was collected from this solution (170 mg, 0.292 mmol, 57%): ^{1}H NMR (C_6D_6) δ 7.92 (s, J = 7.6, 4H, Ph), 7.18–7.13 (m, 6H, Ph), 6.65 (s, 1H, $(OC(Ph))_2CH$), 5.60 (d, J = 5.4, 2H, $MeC_6H_4CHMe_2$), 5.22 (d, J = 5.4, 2H, $MeC_6H_4CHMe_2$), 2.67 (sept, J = 7.0, 1H, $MeC_6H_4CHMe_2$), 1.95 (s, 3H, $MeC_6H_4CHMe_2$), 1.18 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 181.2 ($(OC(Ph))_2CH$), 139.7 (*ipso*-Ph), 131.1 (Ph), 128.5 (Ph), 127.5 (Ph), 95.8 (J_{CH} = 158, $(OC(Ph))_2CH$), 89.0 (C5), 88.2 (C2), 74.8 (C3 or C4), 69.6 (C3 or C4), 31.7 (C6), 22.8 (C7), 17.9 (C1); IR (KBr) 3084 (w), 3062 (w), 2967 (m), 2926 (m), 2876 (w), 1591 (m), 1541 (s), 1523 (s), 1482 (s), 1455 (m), 1396 (m), 1378 (s), 1314 (m), 1233 (m), 1024 (w), 747 (m), 715 (m), 688 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{25}ClO_2Os$: C, 51.49; H, 4.32. Found: C, 51.30; H, 4.38.

CymOs[(OC(Me))$_2$CH](O$_2$CMe) (21). A stirred solution of **19** (20 mg, 0.044 mmol) in acetone (3 mL) was treated with AgO_2CMe (7.7 mg, 0.046 mmol). The solvent was removed *in vacuo* after 17 h of stirring. The solid residue was washed with pentane (1 mL), extracted into toluene, and filtered through Celite. The solvent was removed from the filtrate under reduced pressure, leaving 20 mg (0.041 mmol, 94%) of a yellow solid: ^{1}H NMR (C_6D_6) δ 5.97 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 5.61 (d, J = 5.6, 2H, $MeC_6H_4CHMe_2$), 5.08 (s, J_{CH}(^{13}C satellites) = 159, 1H, $(OC(Me))_2CH$), 2.60 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 2.23 (s, 3H, O_2CMe), 1.92 (s, 3H, $MeC_6H_4CHMe_2$), 1.73 (s, 6H, $(OC(Me))_2CH$), 1.15 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 185.6 ($(OC(Me))_2CH$), 176.5 (O_2CMe), 99.7 ($(OC(Me))_2CH$), 87.8 (C5), 86.1 (C2), 72.9 (C3 or C4), 68.7 (C3 or C4), 31.7 (C6), 26.9 ($(OC(Me))_2CH$), 23.7 (O_2CMe), 22.7 (C7), 17.1 (C1); IR (KBr) 3041 (w), 2974 (m), 2960 (m), 2873 (w), 1626 (s), 1579 (s), 1522 (s), 1429 (m), 1373 (s), 1363 (s), 1315 (s), 1277 (m), 1016 (m), 673 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_4Os$: C, 42.31; H, 5.01. Found: C, 42.23; H, 5.07.

CymOs[CH(CO$_2$Me)$_2$][(OC(Me))$_2$CH] (22). Treatment of **17** (15 mg, 0.29 mmol) with $H_2C(COMe)_2$ (6.6 mg, 0.066 mmol) in C_6D_6 (0.7 mL) resulted in an immediate color change to yellow. A ^{1}H NMR spectrum obtained after 10 min showed a new compound and H_2N-*t*-Bu. The solvent was lyophilized and the solid residue was extracted into pentane and filtered through Celite. The solvent was removed from the filtrate under reduced pressure, leaving 14 mg (0.026 mmol, 90%) of a bright yellow solid: ^{1}H NMR (C_6D_6) δ 5.46 (d, J = 5.7, 2H, $MeC_6H_4CHMe_2$), 5.44 (d, J = 5.2, 2H, $MeC_6H_4CHMe_2$), 5.10 (s, 1H, $(OC(Me))_2CH$), 4.17 (s, 1H, $CH(CO_2Me)_2$), 3.39 (s, 6H, $CH(CO_2Me)_2$), 2.51 (sept,

J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.79 (s, 3H, $MeC_6H_4CHMe_2$), 1.69 (s, 6H, $(OC(Me))_2CH$), 1.09 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 185.6 ($(OC(Me))_2CH$), 174.7 ($CH(CO_2Me)_2$), 100.9 (J_{CH} = 159, $(OC(Me))_2CH$), 90.7 (C5), 81.8 (C2), 77.1 (C3 or C4), 73.4 (C3 or C4), 49.9 ($CH(CO_2Me)_2$), 31.1 (J_{CH} = 138, $CH(CO_2Me)_2$), 30.5 (C6), 26.9 ($(OC(Me))_2CH$), 22.3 (C7), 16.4 (C1); IR (KBr) 3062 (w), 2964 (m), 2945 (m), 2924 (m), 2875 (w), 1720 (s), 1572 (s), 1527 (m), 1435 (m), 1394 (m), 1182 (m), 1120 (m), 1068 (m), 800 (m) cm^{-1}. HREIMS: calcd for $C_{20}H_{28}O_6{}^{192}Os$ (M^+), 556.1501; found, 556.1511.

CymOs[CH(CO$_2$Me)$_2$][(OC(Ph))$_2$CH] (23). Treatment of 17 (8.4 mg, 0.21 mmol) with $H_2C(COPh)_2$ (5.0 mg, 0.022 mmol) in C_6D_6 (0.7 mL) resulted in an immediate color change to bright red. A ^1H NMR spectrum obtained after 5 min showed a new compound and H_2N-t-Bu. The solvent was lyophilized, and the solid residue was washed with pentane (1 mL), extracted into Et_2O, and filtered through Celite. The solvent was removed from the filtrate under reduced pressure leaving 8.2 mg (0.012 mmol, 58%) of a red solid: ^1H NMR (C_6D_6) δ 7.90 (s, J = 6.9, 4H, Ph), 7.22–7.16 (m, 6H, Ph), 6.63 (s, 1H, $(OC(Ph))_2(CH)$, 5.56 (d, J = 5.5, 2H, $MeC_6H_4CHMe_2$), 5.46 (d, J = 5.5, 2H, $MeC_6H_4CHMe_2$), 4.47 (s, 1H, $CH(CO_2Me)_2$), 3.36 (s, 6H, $CH(CO_2Me)_2$), 2.59 (sept, J = 6.9, 1H, $MeC_6H_4CHMe_2$), 1.90 (s, 3H, $MeC_6H_4CHMe_2$), 1.14 (d, J = 6.9, 6H, $MeC_6H_4CHMe_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 180.2 ($(OC(Ph))_2CH$), 174.9 ($CH(CO_2Me)_2$), 139.7 (*ipso*-Ph), 131.0 (Ph), 128.4 (Ph), 127.3 (Ph), 113.3 (J_{CH} = 158, $(OC(Ph))_2CH$), 95.8 (C5), 91.8 (C2), 78.3 (C3 or C4), 73.9 (C3 or C4), 50.0 ($CH(CO_2Me)_2$), 31.7 (J_{CH} = 138, $CH(CO_2Me)_2$), 30.3 (C6), 22.4 (C7), 16.8 (C1); IR (KBr) 3064 (w), 2958 (m), 2941 (m), 2920 (m), 2850 (w), 1720 (s), 1591 (m), 1539 (s), 1524 (s), 1485 (m), 1452 (m), 1432 (m), 1390 (m), 1196 (m), 1115 (m), 1059 (m) cm^{-1}. HREIMS: calcd for $C_{30}H_{32}O_6{}^{192}Os$ (M^+), 680.1814; found, 680.1812.

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