

and  $(C_6H_5CH_2)_2NH$  are summarized in Table I. These spectra show the distinctive differences between a dialkyltriazanium salt and its parent amine. The bands in the range 3300–3100  $cm^{-1}$  are indicative of  $NH_2$  stretching, that at 1600  $cm^{-1}$  is indicative of  $NH_2$  bending, and that at 900  $cm^{-1}$  is indicative of CNC stretching. The band between 1110 and 1100  $cm^{-1}$  does not show

in the amines but is fairly strong in the triazanium salts. One might tentatively assign this band to N–N–N stretching.

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## Polymeric Ruthenium(I) and Binuclear Ruthenium(I) and Osmium(I) Carboxylate-Bridged Complexes Containing Diphosphine, Diarsine, Arsinophosphine, Diphosphine Chalcogenide, and Dithioether Ligands: The Structure of $[Ru_2(CO)_4(\mu-O_2CMe)_2(MeSCH_2SMe)]_2 \cdot THF$

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The addition of 1 molar equiv of the bidentate ligands  $L\bar{L}$ ,  $R'_2P(CH_2)_nPR'_2$ ,  $R'_2As(CH_2)_nAsR'_2$ ,  $Ph_2P(CH_2)_2AsPh_2$ ,  $Ph_2PCH_2P(S)Ph_2$ ,  $Ph_2P(S)CH_2P(S)Ph_2$ , and  $R'SCH_2SR'$  ( $R' = Me, Ph; n = 1-4$ ), to THF/acetone solutions of either the polymer  $[Ru_2(CO)_4(\mu-O_2CMe)_2]_n$  or the dimers  $[Ru_2(CO)_4(\mu-O_2CR)_2(NCMe)_2]$  ( $R = Me, Et$ ) affords a new class of polymeric species,  $[Ru_2(CO)_4(\mu-O_2CR')_2(L\bar{L})]_n$ , in which the carboxylate-bridged dimeric units are linked by the bidentate  $L\bar{L}$  ligands. The use of 2 molar equiv of either  $Ph_2PCH_2PPh_2$  (dppm) or  $Ph_2PCH_2P(S)Ph_2$  (dppmS) in the reaction with the acetate-bridged dimer yields complexes of the type  $[Ru_2(CO)_4(\mu-O_2CMe)_2(\eta^1-Ph_2PCH_2P(X)Ph_2)]_2$  ( $X = S$ , electron pair). The osmium analogues  $[Os_2(CO)_4(\mu-O_2CMe)_2(\eta^1-Ph_2PCH_2P(X)Ph_2)]_2$  can be obtained by heating  $[Os_2(CO)_6(\mu-O_2CMe)_2]$  with 2 equiv of dppm or dppmS in  $CHCl_3$ . The pendant  $PPh_2$  moieties of  $[Os_2(CO)_4(\mu-O_2CMe)_2(\eta^1-dppm)]_2$  can be oxidized to  $P(O)Ph_2$  groups by treatment with 2 molar equiv of  $H_2O_2$ . The structure of the dithioether species  $[Ru_2(CO)_4(\mu-O_2CMe)_2(MeSCH_2SMe)]_2 \cdot THF$  has been determined by an X-ray diffraction study and has been shown to consist of a polymeric chain of  $[Ru_2(CO)_4(\mu-O_2CMe)_2]$  units linked by  $MeSCH_2SMe$  ligands. Each dimer unit has a sawhorse-like arrangement in which the four carbonyls are opposite the bridging acetate groups. The independent Ru–Ru bonds are 2.682 (1) and 2.684 (1) Å. This compound crystallizes in the space group  $P\bar{1}$  with  $a = 15.838$  (2) Å,  $b = 17.562$  (2) Å,  $c = 8.238$  (2) Å,  $\alpha = 102.55$  (1)°,  $\beta = 101.87$  (1)°,  $\gamma = 68.17$  (1)°,  $V = 2056.3$  Å<sup>3</sup>, and  $Z = 2$ . The asymmetric unit contains two  $[Ru_2(CO)_4(\mu-O_2CMe)_2(MeSCH_2SMe)]$  moieties. On the basis of 3533 unique observations and 435 parameters varied, the structure was refined to  $R = 0.046$  and  $R_w = 0.055$ .

### Introduction

In previous papers<sup>1,2</sup> we reported the use of the acetate-bridged species  $[Ru_2(CO)_4(\mu-O_2CR)_2]_n$  and  $[Ru_2(CO)_4(\mu-O_2CR)_2(NCMe)_2]$  as convenient synthons for the preparation of an unusual series of binuclear Ru(I) complexes, either through replacement of the carboxylate groups by other bridging anionic ligands<sup>1</sup> or by substitution of the labile groups opposite the Ru–Ru bond by bidentate diphosphine and dithioether ligands.<sup>2</sup> In this paper we describe in detail some of the diphosphine and dithioether chemistry that was outlined in the preliminary communication<sup>2</sup> and also extend this work to include the use of a broader range of diphosphine, arsinophosphine, diarsine, and diphosphine chalcogenide ligands,  $Ph_2P(Y)CH_2P(X)Ph_2$  ( $X = S$ , electron pair;  $Y = O, S, Se$ ), and to include some related chemistry of Os(I).

### Experimental Section

**General Considerations.** All compounds described in this paper were prepared under an atmosphere of dinitrogen by using Schlenk techniques and solvents that were appropriately dried and distilled under dinitrogen immediately before use. The ligands  $Ph_2PCH_2PPh_2$  (dppm),  $Ph_2PCH_2CH_2PPh_2$  (dppe),  $Ph_2PCH_2CH_2CH_2PPh_2$  (dppp),  $Ph_2PCH_2CH_2CH_2CH_2PPh_2$  (dppb),  $Ph_2AsCH_2AsPh_2$  (dpam),  $Ph_2AsCH_2CH_2AsPh_2$  (dpae),  $Ph_2P(CH_2)_2AsPh_2$  (arphos),  $PhSCH_2SPh$ , and  $MeSCH_2SMe$  were purchased from Aldrich Chemicals;  $Me_2PCH_2PMe_2$  (dmpm) was obtained from Strem Chemicals. The compounds  $Ph_2PCH_2P(S)Ph_2$  (dppmS)<sup>3</sup> and  $Ph_2PCH_2P(Se)Ph_2$  (dppmSe)<sup>4</sup> and complexes  $[Ru_2(CO)_4(\mu-O_2CR)_2]_n$  ( $R = Me, Et$ ),<sup>5</sup>  $[Ru_2(CO)_4(\mu-O_2CR)_2(NCMe)_2]$  ( $R = Me, Et$ ),<sup>5</sup>  $[Os_2(CO)_6(\mu-O_2CMe)_2]$ ,<sup>6</sup> and  $[Os_2(CO)_4(\mu-O_2CMe)_2(NCMe)_2]$ <sup>6</sup> were prepared by

literature methods. Infrared spectra were recorded on either a Nicolet 7199 or Mattson Polaris FT IR spectrometer as Nujol mulls on KBr plates or as solutions in 0.1 mm thick sodium chloride cells. The  $^{31}P\{^1H\}$  NMR spectra were recorded on either a Bruker WH-200 (operating at 81.0 MHz), WH-400 (at 161.4 MHz), or AM-300 (at 121.5 MHz) FT spectrometer.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were obtained at 300.1 and 75.5 MHz, respectively, on a Bruker AM-300 instrument. Second-order  $^{31}P\{^1H\}$  NMR spectra were analyzed by computer simulation using the PANIC program supplied by Bruker. Chemical shifts are reported relative to external  $H_3PO_4$  ( $^{31}P$ ) and external  $SiMe_4$  ( $^1H$  and  $^{13}C$ ). Either  $C_6D_6$  or  $CDCl_3$  was used as the NMR solvent, and in each case, the deuterium resonance served as the lock for the spectrometers. For all nuclei, positive chemical shifts lie downfield from the standard. Elemental analyses were performed by the microanalytical departments at the University of Alberta and CSIR.

**Preparation of the Metal Complexes.** (1)  $[Ru_2(CO)_4(\mu-O_2CR)_2(L\bar{L})]_n$  (1–10). For these complexes,  $R = Me$  for 1, 2, and 5–10,  $R = Et$  for 3 and 4, and  $L\bar{L} = Me_2PCH_2PMe_2$  (1, 3),  $Ph_2PCH_2PPh_2$  (2, 4),  $Ph_2PCH_2CH_2PPh_2$  (5),  $Ph_2PCH_2CH_2CH_2PPh_2$  (6),  $Ph_2PCH_2CH_2CH_2CH_2PPh_2$  (7),  $Ph_2AsCH_2AsPh_2$  (8),  $Ph_2AsCH_2CH_2AsPh_2$  (9), and  $Ph_2P(CH_2)_2AsPh_2$  (10).

**Method A.** Typically, a suspension of the acetate-bridged polymer  $[Ru_2(CO)_4(\mu-O_2CMe)_2]_n$  and 1 molar equiv (per dimer unit) of the appropriate diphosphine, diarsine, or arsinophosphine were heated under reflux in 20 mL of THF for 4–6 h. Gradually, the starting polymer disappeared and a clear yellow solution formed. Upon cooling, a yellow

- (1) Cowie, M.; Sherlock, S. J.; Singleton, E.; Steyn, M. M. d. V. *J. Organomet. Chem.* **1989**, *361*, 353.
- (2) Cowie, M.; Sherlock, S. J.; Singleton, E.; Steyn, M. M. d. V. *Organometallics* **1988**, *7*, 1663.
- (3) Grim, S. O.; Mitchell, J. D. *Inorg. Synth.* **1976**, *16*, 195.
- (4) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.
- (5) Crooks, G. R.; Gamlen, G.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 2761.
- (6) Deeming, A. J.; Hursthouse, M. B.; Randle, N. P.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2473.

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**Table I.**  $^{31}\text{P}\{^1\text{H}\}$  NMR Data for the Phosphorus-Containing Ru(I) and Os(I) Complexes and the  $\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{P}(\text{Y})\text{Ph}_2$  Ligands (X = S, Electron Pair; Y = O, S, Electron Pair)

compd	spin system	$\delta_{\text{PA}}^a$ ppm	$\delta_{\text{PX}}^a$ ppm	$^2J(\text{PA}-\text{CH}_2-\text{PX})$ , Hz	$^3J(\text{P}-\text{M}-\text{M}-\text{P})$ , Hz
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{dmpm})]_n$ (1)	A	-7.55 <sup>b</sup>			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{dppm})]_n$ (2)	A	14.90 <sup>b</sup>			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{dmpm})]_n$ (3)	A	-4.02			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{dppm})]_n$ (4)	A	14.97 <sup>b</sup>			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{dppe})]_n$ (5)	A	19.63			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{dppp})]_n$ (6)	A	11.06			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{dppb})]_n$ (7)	A	22.20			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{arphos})]_n$ (10)	A	18.36 (s), 17.92 (s), 17.48 (s)			
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]_n$ (15)	X		34.54		
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppm})_2]$ (17)	AA'XX'	14.87	-26.32	63	114
$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppmS})_2]$ (18)	AA'XX'	11.57	34.30	28	123
$[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppmS})_2]$ (19)	AA'XX'	14.09	34.19	25	69
$[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppm})_2]$ (20)	AA'XX'	17.27	-27.05	72	60
$[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppmO})_2]$ (21)	AA'XX'	13.88	24.23	23	68
$[\text{Ph}_2\text{P}_X(\text{S})\text{CH}_2\text{P}_X(\text{S})\text{Ph}_2]$	X		34.60		
$[\text{Ph}_2\text{P}_A\text{CH}_2\text{P}_A\text{Ph}_2]$	A	-23.0			
$[\text{Ph}_2\text{P}_A\text{CH}_2\text{P}_X(\text{S})\text{Ph}_2]$	AX	-27.85	40.32	76	
$[\text{Ph}_2\text{P}_A\text{CH}_2\text{P}_X(\text{O})\text{Ph}_2]$	AX	-28.72	27.41	50	

<sup>a</sup> Chemical shifts are quoted relative to  $\text{H}_3\text{PO}_4$ . The NMR solvent for all complexes was  $\text{CDCl}_3$ . <sup>b</sup> Spectrum was recorded at  $-40^\circ\text{C}$ .

solid was deposited on the bottom of the reaction vessel. Complete precipitation of the product was brought about through the addition of 20 mL of hexane. Yields ranged from 40 to 70%.

**Method B.** A solution of the selected diphosphine or diarsine (1.0 mmol) in either 15 mL of THF or 15 mL of acetone was added to a stirred orange-yellow solution of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{NCMe})_2]$  (1.0 mmol) (R = Me, Et) in 30 mL of THF or acetone. An immediate color change from orange to yellow was observed upon addition of the ligand solution. Stirring was continued at room temperature in most cases for 16 h. During this time a pale yellow solid precipitated from solution. In general, the diphosphines (and diarsines) having the smallest number of bridging carbon atoms (e.g. dppm and dpam) tended to precipitate immediately, while the higher molecular weight diphosphines often required several hours to precipitate. The yellow products were filtered out, washed with ether ( $2 \times 20$  mL), and dried under vacuum. Yields ranged from 95% for  $\text{L}=\text{L}$  = dppm to 20% for  $\text{L}=\text{L}$  = dpbb. The compounds  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{L}=\text{L})]_n$  (R = Me, Et;  $\text{L}=\text{L}$  = dmpm, dppm, dpam, dpae, arphos) were only sparingly soluble in typical organic solvents whereas  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{L}=\text{L})]_n$  ( $\text{L}=\text{L}$  = dppe, dppp, dpbb) were moderately soluble in dichloromethane and chloroform.  $^{31}\text{P}\{^1\text{H}\}$  NMR data are presented in Table I; IR and  $^1\text{H}$  NMR data are given as supplementary material. The analytical data for these complexes are listed below.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Me}_2\text{PCH}_2\text{PMe}_2)]_n$  (1): bright yellow solid. Anal. Calcd for  $\text{C}_{13}\text{H}_{20}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 27.47; H, 3.55. Found: C, 27.21; H, 3.77.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]_n$  (2): yellow solid. Anal. Calcd for  $\text{C}_{33}\text{H}_{28}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 48.13; H, 3.50. Found: C, 48.53; H, 3.45.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{Me}_2\text{PCH}_2\text{PMe}_2)]_n$  (3): yellow solid. Anal. Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 31.04; H, 4.02. Found: C, 30.71; H, 4.19.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]_n$  (4): yellow solid. Anal. Calcd for  $\text{C}_{35}\text{H}_{32}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 49.76; H, 3.70. Found: C, 50.09; H, 4.16.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]_n$  (5): yellow solid. Anal. Calcd for  $\text{C}_{34}\text{H}_{30}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 49.16; H, 3.64. Found: C, 48.94; H, 3.27.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]_n$  (6): yellow solid. Anal. Calcd for  $\text{C}_{35}\text{H}_{32}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 49.77; H, 3.82. Found: C, 48.90; H, 3.75.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]_n$  (7): yellow solid. Anal. Calcd for  $\text{C}_{36}\text{H}_{34}\text{O}_8\text{P}_2\text{Ru}_2$ : C, 50.35; H, 3.99. Found: C, 49.94; H, 3.49.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{AsCH}_2\text{AsPh}_2)]_n$  (8): yellow solid. Anal. Calcd for  $\text{As}_2\text{C}_{33}\text{H}_{28}\text{O}_8\text{Ru}_2$ : C, 43.82; H, 3.12. Found: C, 44.32; H, 3.26.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)]_n$  (9): yellow solid. Anal. Calcd for  $\text{As}_2\text{C}_{34}\text{H}_{30}\text{O}_8\text{Ru}_2$ : C, 44.50; H, 3.29. Found: C, 43.80; H, 3.17.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2)]_n$  (10): yellow solid. Anal. Calcd for  $\text{AsC}_{34}\text{H}_{30}\text{O}_8\text{PRu}_2$ : C, 46.69; H, 3.46. Found: C, 46.69; H, 3.18.

(2)  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{R}'\text{SCH}_2\text{SR}')_n$  (11-14). For these complexes, R = Me for 11 and 13, R = Et for 12 and 14, R' = Me for 11 and 12, and R' = Ph for 13 and 14. The dithioether-linked polymers could not be synthesized by method A but were all prepared by method

B described above. The colors, yields, and analytical data for the dithioether-linked polymers are given below.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})]_n$  (11): yellow crystalline solid; yield 95%. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_8\text{Ru}_2\text{S}_2$ : C, 24.45; H, 2.69; S, 11.85. Found: C, 25.06; H, 2.69; S, 10.24.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{MeSCH}_2\text{SMe})]_n$  (12): yellow crystalline solid; yield 95%. Anal. Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_8\text{Ru}_2\text{S}_2$ : C, 27.46; H, 3.17; S, 9.00. Found: C, 27.35; H, 3.61; S, 8.62.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{PhSCH}_2\text{SPh})]_n$  (13): yellow solid; yield 90%. Anal. Calcd for  $\text{C}_{21}\text{H}_{18}\text{O}_8\text{Ru}_2\text{S}_2$ : C, 37.95; H, 2.71. Found: C, 37.94; H, 3.34.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{PhSCH}_2\text{SPh})]_n$  (14): yellow crystalline solid; yield 80%. Anal. Calcd for  $\text{C}_{23}\text{H}_{22}\text{O}_8\text{Ru}_2\text{S}_2$ : C, 39.88; H, 3.18; S, 9.26. Found: C, 39.46; H, 3.34; S, 9.00.

(3)  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{Ph}_2\text{P}(\text{X})\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (15, 16). For these complexes, R = Me and X = electron pair for 16 and R = Et and X = S for 15. These polymeric species were also prepared by using the procedure as described in method B.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CEt})_2(\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (15): orange-yellow crystalline solid; yield 54%. Anal. Calcd for  $\text{C}_{35}\text{H}_{32}\text{O}_8\text{P}_2\text{Ru}_2\text{S}_2$ : C, 46.25; H, 3.55. Found: C, 46.38; H, 3.73.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (16): orange-yellow solid; yield 79%. Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{O}_8\text{P}_2\text{Ru}_2\text{S}_2$ : C, 46.70; H, 3.33. Found: C, 46.83; H, 3.53.

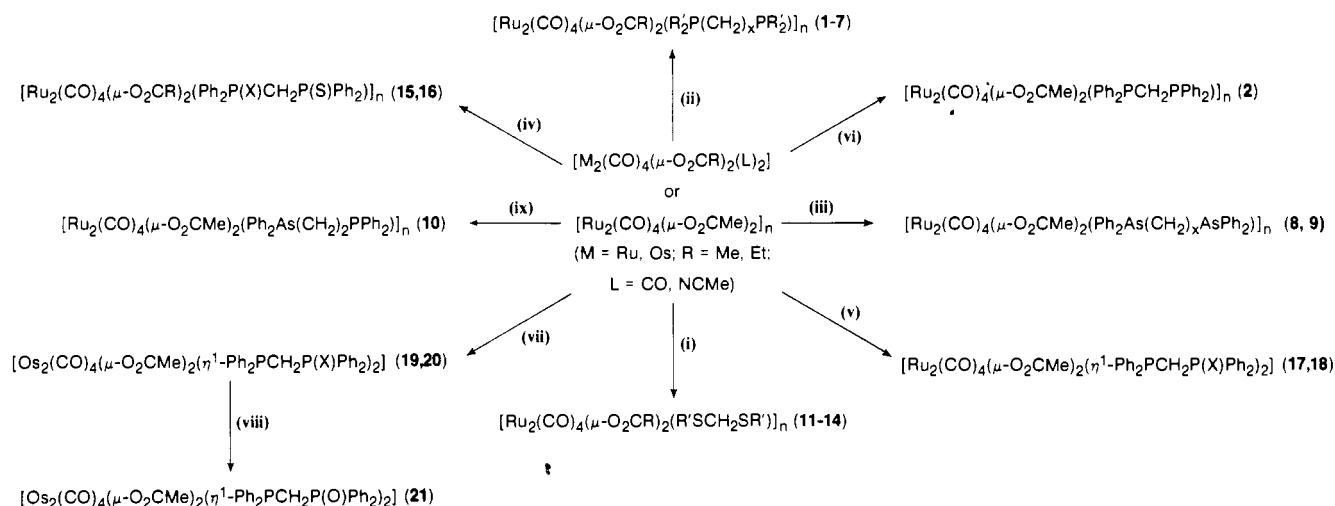
(4)  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2)]_n$  (17, 18). For these complexes, X = electron pair for 17 and X = S for 18. Typically, 2 molar equiv of dppm or dppmS was added as a solid to a stirred solution of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{NCMe})_2]$  in 10 mL of THF. After 2 h of stirring, the solvent was removed under vacuum and the remaining yellow residue was extracted with 1 mL of THF. The addition of hexane (20 mL) caused the immediate precipitation of a yellow solid, which was isolated from the pale yellow supernatant and kept under vacuum for several hours.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]_n$  (17): bright yellow solid; yield 83%. Anal. Calcd for  $\text{C}_{58}\text{H}_{50}\text{O}_8\text{P}_4\text{Ru}_2$ : C, 58.00; H, 4.20. Found: C, 58.09; H, 4.41.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (18): yellow solid; yield 42%. Anal. Calcd for  $\text{C}_{58}\text{H}_{50}\text{O}_8\text{P}_4\text{Ru}_2\text{S}_2$ : C, 55.06; H, 3.98. Found: C, 55.83; H, 3.77.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]_n$  (17) was also prepared from the acetate-bridged polymer  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2]_n$  as follows. A suspension of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2]_n$  (0.440 g, 2.0 mmol) and dppm (0.760 g, 2.0 mmol) was heated under reflux in THF (40 mL) for 2 h, during which time the solid material disappeared, leaving a yellow solution. The reaction mixture was filtered and the solvent removed under vacuum. Extraction with  $\text{CH}_2\text{Cl}_2$  (20 mL) and addition of MeOH (40 mL) to the extract afforded  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]_n$  (0.500 g) as a yellow crystalline solid upon evaporation of the  $\text{CH}_2\text{Cl}_2$ . Yield: 42%. Anal. Calcd for  $\text{C}_{58}\text{H}_{50}\text{O}_8\text{P}_4\text{Ru}_2$ : C, 58.00; H, 4.20. Found: C, 57.07; H, 3.87.

(5)  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (19).  $\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$  (0.156 g, 0.375 mmol) and  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2]$  (0.125 g, 0.188 mmol) were dissolved in 20 mL of  $\text{CHCl}_3$ . The mixture was heated under reflux for 1.5 h, during which time the solution changed from

Scheme 1<sup>a</sup>

<sup>a</sup>Key: (i) 1 equiv of R'SCH<sub>2</sub>SR' (R' = Me, Ph), where R = Me, Et, M = Ru, and L = NCMe; (ii) 1 equiv of R'<sub>2</sub>P(CH<sub>2</sub>)<sub>x</sub>PR'<sub>2</sub> (x = 1-4; R' = Ph, Me), where R = Me, Et, M = Ru, and L = NCMe, or 1 equiv of R'<sub>2</sub>P(CH<sub>2</sub>)<sub>x</sub>PR'<sub>2</sub> (x = 1-4, R' = Ph), when [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>]<sub>n</sub> is used; (iii) 1 equiv of Ph<sub>2</sub>As(CH<sub>2</sub>)<sub>x</sub>AsPh<sub>2</sub> (x = 1 or 2, R = Me), where R = Me, M = Ru, and L = NCMe; (iv) 1 equiv of Ph<sub>2</sub>P(X)CH<sub>2</sub>P(S)Ph<sub>2</sub> (X = S, electron pair), where R = Me for X = electron pair, R = Et for X = S, M = Ru, and L = NCMe; (v) 2 equiv of Ph<sub>2</sub>PCH<sub>2</sub>P(X)Ph<sub>2</sub> (X = S, electron pair), where R = Me, M = Ru, and L = NCMe; (vi) 2 equiv of Ph<sub>2</sub>PCH<sub>2</sub>P(Se)Ph<sub>2</sub>, where R = Me, M = Ru, and L = NCMe; (vii) 2 equiv of Ph<sub>2</sub>PCH<sub>2</sub>P(X)Ph<sub>2</sub> (X = S, electron pair), where R = Me, M = Os, and L = CO; (viii) 2 equiv of H<sub>2</sub>O<sub>2</sub> (for X = electron pair); (ix) 1 equiv of Ph<sub>2</sub>As(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>, where R = Me, M = Ru, and L = NCMe.

colorless to yellow. After cooling, the solvent was removed under vacuum and the pale yellow residue was extracted with THF (1 mL). Addition of 20 mL of hexane caused the immediate precipitation of [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>P(S)Ph<sub>2</sub>)<sub>2</sub>] (0.238 g, 0.165 mmol, 88% yield) as a pale yellow solid. Anal. Calcd for C<sub>58</sub>H<sub>50</sub>O<sub>8</sub>Os<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 48.26; H, 3.91. Found: C, 48.65; H, 3.95.

(6) [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (20). This compound was prepared by using a procedure identical to that described above for the synthesis of [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-dppmS)<sub>2</sub>] (19), with the exception that dppm was used in place of dppmS. Yield of pale yellow crystalline solid: 88%. Anal. Calcd for C<sub>58</sub>H<sub>50</sub>O<sub>8</sub>Os<sub>2</sub>P<sub>4</sub>: C, 50.51; H, 3.65. Found: C, 49.63; H, 3.92.

(7) [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)<sub>2</sub>] (21). A 0.030-mL volume of 30% H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O was syringed into a stirred pale yellow solution of [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (20) (0.150 g, 0.109 mmol) in a mixture of 30 mL of acetone and 6 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 2 h with no apparent change in color. The solvent was removed under vacuum, leaving a viscous, pale yellow solid, which was redissolved in 1 mL of THF. Addition of 20 mL of Et<sub>2</sub>O caused the immediate precipitation of [Os<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(η<sup>1</sup>-Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)<sub>2</sub>] (0.103 g, 0.073 mmol, 67% yield) as a colorless solid. Anal. Calcd for C<sub>58</sub>H<sub>50</sub>O<sub>10</sub>Os<sub>2</sub>P<sub>4</sub>: C, 49.36; H, 3.57. Found: C, 49.07; H, 3.84.

**Reaction of 1 molar equiv of Ph<sub>2</sub>PCH<sub>2</sub>P(Se)Ph<sub>2</sub> with [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(NCMe)<sub>2</sub>].** Ph<sub>2</sub>PCH<sub>2</sub>P(Se)Ph<sub>2</sub> (0.225 g, 0.486 mmol) was added as a solid to a stirred orange-yellow solution of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(NCMe)<sub>2</sub>] (0.250 g, 0.486 mmol) in 10 mL of THF. The mixture was stirred for 2 h, during which time a rust-colored solid precipitated from solution. The precipitate was allowed to settle, washed with hexane (20 mL), and dried overnight under vacuum. <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed that the only phosphorus-containing compound was [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (2). The red-brown color resulted from contamination by selenium, which was released as a byproduct of the polymerization reaction. The yield of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] (2) was essentially quantitative.

**X-ray Data Collection and Structure Solution.** Yellow crystals of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(MeSCH<sub>2</sub>SMe)<sub>2</sub>·THF (11), suitable for X-ray data collection, were grown by slow diffusion of Et<sub>2</sub>O into a THF solution of the complex at 23 °C. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation up to 2θ = 50.0°. The automatic peak search, reflection indexing, and cell reduction programs established the space group as P1 or P1̄, and the successful refinement of the structure in P1̄ suggested that it was correct. Lorentz and polarization corrections were applied to the data, which were also corrected for absorption by using the method of Walker and Stuart.<sup>7,8</sup> Three standard reflections were measured every

**Table II.** Crystallographic Data for [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(MeSCH<sub>2</sub>SMe)<sub>2</sub>·THF (11)

C <sub>26</sub> H <sub>36</sub> O <sub>17</sub> Ru <sub>4</sub> S <sub>4</sub>	fw: 1153.10
a = 15.838 (2) Å	space group: P1̄
b = 17.562 (2) Å	T = 22 °C
c = 8.238 (2) Å	λ = 0.71073 Å
α = 102.55 (1)°	ρ <sub>calcd</sub> = 1.862 g·cm <sup>-3</sup>
β = 101.87 (1)°	μ = 16.72 cm <sup>-1</sup>
γ = 68.17 (1)°	transm coeff = 0.786-1.144
V = 2056.3 Å <sup>3</sup>	R = 0.046
Z = 2	R <sub>w</sub> = 0.055

60 min of exposure to check crystal orientation and stability during the course of data collection. No significant deterioration in these standards was observed. See Table II for a summary of data collection details. The heavy-atom positions were obtained through the use of MULTAN; all other atoms were located by the useful sequence of full-matrix least-squares refinement and difference Fourier techniques. All non-hydrogen atoms (with the exception of the cocrystallized THF molecule) were refined anisotropically, while the hydrogen atoms were placed in idealized positions, derived from the observed positions and assuming an idealized hybridization at the carbon atoms, by using C-H distances of 0.95 Å and were not refined. The hydrogen thermal parameters were fixed at 1.2 times those of the attached carbon atoms. Although the THF molecule could be located, it is apparently rotationally disordered since none of the five atoms refined successfully as an oxygen. For this reason all five atoms of this group were refined as carbons. Fractional atomic coordinates are collected in Table III. Selected bond lengths and angles can be found in Tables IV and V. Scattering factors, anomalous dispersion terms, and other details of refinement have been described previously.<sup>1</sup>

## Results

The spectroscopic data for all of the compounds are presented in the Discussion and are tabulated in Table I and in the supplementary material. The observed chemical transformations are summarized in Scheme I. An X-ray structure was determined for compound 11 and is presented below.

## Discussion

(a) **Description of the Structure of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>(MeSCH<sub>2</sub>SMe)<sub>2</sub>·THF (11).** The structure determination of compound 11 confirms the polymeric nature of this species and, on the basis of the similarity in spectral parameters (vide infra), suggests analogous structures for complexes 1-16. A view of one

(7) Stewart, D.; Walker, N. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 1581.

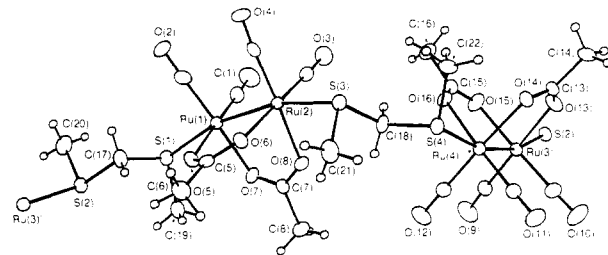
(8) Programs used for solution and refinement of the structure were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

**Table III.** Positional and Thermal Parameters for the Atoms of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})_2]\cdot\text{THF}$  (11)<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup> <sup>b</sup>
Ru(1)	-0.08667 (6)	-0.24095 (6)	0.0988 (1)	3.08 (2)
Ru(2)	0.08458 (6)	-0.35122 (6)	0.1015 (1)	2.86 (2)
Ru(3)	0.53957 (7)	-0.19568 (6)	0.5272 (1)	3.30 (2)
Ru(4)	0.48580 (6)	-0.30372 (6)	0.2833 (1)	3.06(2)
S(1)	-0.2372 (2)	-0.1298 (2)	0.0308 (4)	4.04 (9)
S(2)	-0.4111 (2)	-0.1166 (2)	-0.2052 (4)	4.00 (9)
S(3)	0.2429 (2)	-0.4396 (2)	0.0408 (4)	3.60 (8)
S(4)	0.4284 (2)	-0.4171 (2)	0.1190 (4)	3.55 (8)
O(1)	-0.0689 (8)	-0.1823 (7)	0.468 (1)	7.4 (4)
O(2)	-0.1669 (6)	-0.3615 (5)	0.155 (1)	6.5 (3)
O(3)	0.1423 (7)	-0.3088 (6)	0.468 (1)	6.3 (3)
O(4)	0.0456 (6)	-0.4894 (5)	0.197 (1)	5.7 (2)
O(5)	-0.0964 (5)	-0.2834 (5)	-0.1612 (9)	4.1 (2)
O(6)	0.0421 (5)	-0.3786 (5)	-0.1565 (9)	3.5 (2)
O(7)	-0.0273 (5)	-0.1625 (5)	0.044 (1)	4.6 (2)
O(8)	0.1131 (5)	-0.2564 (4)	0.027 (1)	4.1 (2)
O(9)	0.4087 (8)	-0.0390 (6)	0.413 (2)	8.6 (4)
O(10)	0.6735 (7)	-0.1809 (7)	0.344 (1)	8.6 (3)
O(11)	0.6085 (6)	-0.3196 (6)	0.039 (1)	6.0 (3)
O(12)	0.3422 (7)	-0.1657 (6)	0.122 (1)	6.3 (3)
O(13)	0.6355 (6)	-0.3039 (5)	0.613 (1)	5.0 (3)
O(14)	0.5929 (5)	-0.3955 (5)	0.410 (1)	3.8 (2)
O(15)	0.4498 (6)	-0.2143 (5)	0.659 (1)	5.1 (2)
O(16)	0.4055 (5)	-0.3038 (5)	0.4587 (9)	3.7 (2)
C(1)	-0.0763 (9)	-0.2045 (8)	0.324 (2)	4.6 (4)
C(2)	-0.1375 (9)	-0.3137 (8)	0.136 (2)	4.5 (4)
C(3)	0.1195 (8)	-0.3741 (7)	0.326 (1)	3.7 (3)
C(4)	0.0577 (8)	-0.4353 (7)	0.159 (1)	3.6 (3)
C(5)	-0.0338 (8)	-0.3416 (7)	-0.233 (1)	3.4 (3)
C(6)	-0.0542 (9)	-0.3662 (9)	-0.419 (2)	5.1 (4)
C(7)	0.0527 (8)	-0.1866 (7)	0.006 (1)	3.7 (3)
C(8)	0.081 (1)	-0.1280 (8)	-0.066 (2)	6.2 (4)
C(9)	0.4570 (9)	-0.1006 (7)	0.453 (2)	4.8 (4)
C(10)	0.6208 (9)	-0.1855 (8)	0.411 (2)	5.3 (4)
C(11)	0.5615 (8)	-0.3126 (7)	0.133 (1)	3.5 (3)
C(12)	0.3987 (8)	-0.2205 (8)	0.185 (1)	4.0 (3)
C(13)	0.6427 (8)	-0.3760 (7)	0.538 (1)	3.9 (3)
C(14)	0.7206 (9)	-0.4449 (8)	0.614 (2)	5.0 (4)
C(15)	0.4063 (8)	-0.2641 (7)	0.602 (2)	3.9 (3)
C(16)	0.3527 (9)	-0.2777 (9)	0.717 (2)	5.7 (4)
C(17)	-0.2996 (9)	-0.1857 (8)	-0.124 (2)	5.0 (4)
C(18)	0.3068 (7)	-0.3708 (7)	0.131 (2)	3.8 (3)
C(19)	-0.216 (1)	-0.0734 (9)	-0.100 (2)	7.3 (5)
C(20)	-0.479 (1)	-0.1105 (9)	-0.048 (2)	5.9 (4)
C(21)	0.243 (1)	-0.445 (1)	-0.181 (2)	6.2 (5)
C(22)	0.4599 (9)	-0.4929 (8)	0.255 (2)	5.0 (4)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. Parameters for THF molecule are given in the supplementary material. <sup>b</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$ .

asymmetric unit, which contains two crystallographically independent dimer units each bridged by two acetate groups and linked to adjacent Ru<sub>2</sub> units by MeSCH<sub>2</sub>SMe groups, is shown in Figure 1. Within a polymer chain the acetate-bridged dimeric units have an alternating "up-down" arrangement in which the acetate bridges on one dimer unit are adjacent to the carbonyl groups on the units on either side. The bidentate MeSCH<sub>2</sub>SMe ligands link the dimeric units through the axial sites trans to the Ru-Ru bonds. The average Ru-S bond distance, 2.498 (3) Å, is somewhat longer than expected. By comparison, the nonaxial Ru-S distances in the bis(μ-mercaptobenzothiazolato) complex  $[\text{Ru}_2(\text{CO})_4(\mu\text{-S}_2\text{C}_7\text{NH}_4)_2(\text{NC}_5\text{H}_3)_2]$  average 2.447 (4) Å<sup>9</sup> and have been found in the range 2.419 (1)-2.453 (1) Å in pyridine 2-thiolate derivatives of Ru(II).<sup>10</sup> In addition, the Ru-S distances are even longer than the axial Ru-P distances in the closely related complexes  $[\text{Ru}_2(\text{CO})_4(\mu\text{-N}_2\text{C}_3\text{H}_3)_2(\text{PPh}_3)_2]$  (2.420 (2), 2.428 (2) Å) and



**Figure 1.** ORTEP diagram of one asymmetric unit of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})_2]\cdot\text{THF}$  (11) showing the numbering scheme. Thermal ellipsoids are drawn at the 20% level with the exception of the hydrogen atoms, which are drawn artificially small. The atoms S(2)' and Ru(3)' are related by the symmetry operations  $(1+x, y, 1+z)$  and  $(x-1, y, z-1)$ , respectively. The cocrystallized THF molecule is not shown. Carbonyl carbons have the same number as their attached oxygen.

$[\text{Ru}_2(\text{CO})_4(\mu\text{-NC}_5\text{H}_4\text{O})_2(\text{PPh}_3)_2]$  (2.440 (1), 2.450 (1) Å),<sup>1</sup> despite the fact that phosphorus has a larger covalent radius than sulfur.<sup>11</sup> In other acetate-bridged Ru(I) dimers the bonds involving the metal and the axial ligands have been found to be long, probably due to the large trans influence of the metal-metal bond. The Ru-Ru bond distances in each asymmetric unit (Ru(1)-Ru(2) = 2.682 (1) Å and Ru(3)-Ru(4) = 2.684 (1) Å) are in excellent mutual agreement and closely parallel such distances in other acetate-bridged Ru(I) dimers.<sup>12,13</sup> The geometry about each Ru center deviates only slightly from that expected for an octahedron with all associated angles near 90°, and adjacent octahedra are essentially eclipsed, as shown by the relevant torsion angles (Table V). The CH<sub>2</sub>-S and CH<sub>3</sub>-S bond distances involving the MeSCH<sub>2</sub>SMe ligands range from 1.76 (1) to 1.82 (1) Å, typical of C-S single bonds,<sup>14</sup> and the angles at the central methylene carbon of the dithioether ligand are close to perfect tetrahedral geometry (S-C-S angles 111.5 (6), 114.3 (6)°), indicating that there is little strain in this bridging group. The Ru-Ru-S bond sequence deviates slightly from linearity (average Ru-Ru-S angle 165.77 (8)°), as also observed for Ru-Ru-P<sup>12,15</sup> and Ru-Ru-CO<sup>13</sup> linkages in other acetate-bridged Ru(I) dimers. This tilt appears to result from the small bite of the acetate groups (ca. 2.2 Å) compared with the Ru-Ru distances and results in tilts of the equatorial planes (perpendicular to Ru-S) of 16.1 (8) and 16.1 (9)° at the two dimer units. These values compare well with that observed in a related hydroxypyridinate-bridged complex (16.2 (4)°) in which the hydroxypyridinate ligand has a bite that is comparable, but much less than the 35.8 (1)° observed when the very small-bite pyrazolate ligands bridge two rutheniums.<sup>1</sup> The average O-C-O angle for the bridging acetate ligands, 125 (1)°, is essentially identical with that found for  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{PBu}_3)_2]$ .<sup>12</sup> Similarly, the bond lengths and angles for the carbonyl groups are normal. The THF molecule is reasonably well-behaved in spite of its disorder, and there are no unusual contacts involving this group.

**(b) Description of Chemistry.** The complexes  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{NCMe})_2]$  and  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2]_n$  (R = Me, Et) have previously been shown to react readily with monodentate phosphines to yield species of the type  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{PR}'_3)_2]$  by substitution of the labile groups opposite the Ru-Ru bond.<sup>5</sup> We have found that both classes of compounds also react with 1 molar equiv of the bidentate ligands  $\text{L}^-\text{L}$ ,  $\text{R}'_2\text{P}(\text{CH}_2)_n\text{PR}'_2$  (R' = Me, Ph; n = 1-4),  $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$  (n = 1, 2),  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ ,  $\text{R}'\text{SCH}_2\text{SR}'$  (R' = Me, Ph), or  $\text{Ph}_2\text{P}(\text{X})\text{-CH}_2\text{P}(\text{S})\text{Ph}_2$  (X = S, electron pair), in THF/acetone to afford a new class of Ru(I) species having the stoichiometry  $[\text{Ru}_2\text{-}$

(9) Jeannin, S.; Jeannin, Y.; Lavigne, G. *Transition Met. Chem. (London)* **1976**, *1*, 186.  
(10) Mura, P.; Olby, B. G.; Robinson, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2101.

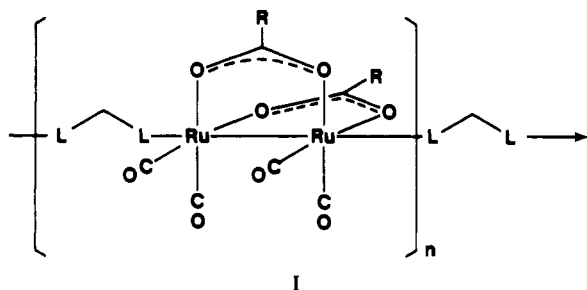
(11) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row Publishing: New York, 1983.  
(12) Opitz, J.; Pickardt, J.; Schumann, H. *J. Organomet. Chem.* **1977**, *128*, 253.  
(13) Spohn, M.; Strähle, J.; Vogt, T. *Z. Naturforsch. B* **1986**, *41*, 1373.  
(14) Hartley, F. R.; Murray, S. G. *Chem. Rev.* **1981**, *81*, 365.  
(15) Gill, D. F.; Mason, R.; Shaw, B. L.; Thomas, K. M. *J. Organomet. Chem.* **1972**, *40*, C67.

Table IV. Intramolecular Bond Distances (Å) in  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})]_2\cdot\text{THF}$  (**11**)<sup>a</sup>

Ru(1)–Ru(2)	2.682 (1)	Ru(4)–O(16)	2.112 (7)	O(8)–C(7)	1.27 (1)
Ru(1)–S(1)	2.504 (3)	Ru(4)–C(11)	1.84 (1)	O(9)–C(9)	1.15 (1)
Ru(1)–O(5)	2.103 (7)	Ru(4)–C(12)	1.80 (1)	O(10)–C(10)	1.13 (1)
Ru(1)–O(7)	2.097 (7)	S(1)–C(17)	1.80 (1)	O(11)–C(11)	1.14 (1)
Ru(1)–C(1)	1.82 (1)	S(1)–C(19)	1.76 (1)	O(12)–C(12)	1.17 (1)
Ru(1)–C(2)	1.85 (1)	S(2)–C(17)	1.82 (1)	O(13)–C(13)	1.26 (1)
Ru(2)–S(3)	2.496 (3)	S(2)–C(20)	1.81 (1)	O(14)–C(13)	1.25 (1)
Ru(2)–O(6)	2.100 (7)	S(3)–C(18)	1.80 (1)	O(15)–C(15)	1.26 (1)
Ru(2)–O(8)	2.113 (7)	S(3)–C(21)	1.81 (1)	O(16)–C(15)	1.24 (1)
Ru(2)–C(3)	1.84 (1)	S(4)–C(18)	1.80 (1)	C(5)–C(6)	1.50 (2)
Ru(2)–C(4)	1.85 (1)	S(4)–C(22)	1.80 (1)	C(7)–C(8)	1.53 (2)
Ru(3)–Ru(4)	2.684 (1)	O(1)–C(1)	1.16 (1)	C(13)–C(14)	1.51 (2)
Ru(3)–O(13)	2.100 (8)	O(2)–C(2)	1.15 (1)	C(15)–C(16)	1.50 (2)
Ru(3)–S(2)'	2.483 (3)	O(3)–C(3)	1.15 (1)	C(23)–C(24)	1.28 (4)
Ru(3)–O(15)	2.105 (8)	O(4)–C(4)	1.16 (1)	C(23)–C(27)	1.36 (3)
Ru(3)–C(9)	1.83 (1)	O(5)–C(5)	1.26 (1)	C(24)–C(25)	1.49 (4)
Ru(3)–C(10)	1.83 (1)	O(6)–C(5)	1.24 (1)	C(25)–C(26)	1.39 (3)
Ru(4)–S(4)	2.508 (3)	O(7)–C(7)	1.26 (1)	C(26)–C(27)	1.66 (3)
Ru(4)–O(14)	2.130 (7)				

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits. THF parameters are given in the supplementary material.

$(\text{CO})_4(\mu\text{-O}_2\text{CR})_2(\text{L}^-\text{L}^-)$ . Although in principle these bidentate groups could bridge two ruthenium atoms to yield isolated binuclear complexes, such a species would require substantial rearrangement of the molecule, and all evidence overwhelmingly suggests that, under the conditions employed, the bidentate ligands instead bridge adjacent dimer units by replacement of the labile axial groups opposite the Ru–Ru bond to give species I, as



diagrammed. These polymeric materials are analogous to the monodentate phosphine adducts, with the exception that the bidentate ligand simultaneously occupies one axial site on one dimer and one on an adjacent dimer. The limited solubility of complexes **1–16** in common organic solvents is consistent with their polymeric formulation, and for some complexes the low solubility precluded their characterization in solution. The IR spectra of these compounds (supplementary material) all display a similar strong–medium–strong–weak pattern of four sharp carbonyl bands between 1900 and 2050  $\text{cm}^{-1}$  along with a strong bridging carboxylate stretch between 1500 and 1600  $\text{cm}^{-1}$ , consistent with a sawhorse-type arrangement in which the cis carbonyl ligands on each metal are trans to the bridging carboxylate oxygens.<sup>12,13</sup> This arrangement of acetates and carbonyls precludes the bridging mode for the bidentate ligands and suggests instead a polymeric structure, which was verified by the structure determination of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})]_2\cdot\text{THF}$  (**11**) (vide supra). The  $^3\text{1P}\{^1\text{H}\}$  NMR spectra of the soluble members of the diphosphine-containing polymers **1–14** and  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{C}^-\text{Et})_2(\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2)]_n$  (**15**) consist of singlets between 35 and –8 ppm (Table I) whereas for  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{arphos})]_n$  (**10**) several singlet resonances appear between 17.48 and 18.36 ppm, which are invariant with temperature, indicating that the phosphorus nuclei are in a variety of different chemical environments. The proton spectra of all soluble polymers (supplementary material) are likewise fairly straightforward and serve mainly to confirm the empirical formula of each compound.

On the basis of these data, a stepwise substitution pathway is suggested in which polymeric compounds are formed via a series of multinuclear intermediates. Thus the variations in solubilities of compounds **1–16** can be accounted for by variations in the chain length of the polynuclear complexes. Osmometric molecular mass

Table V. Selected Angles (deg) in  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{MeSCH}_2\text{SMe})]_2\cdot\text{THF}$  (**11**)<sup>a</sup>

Bond Angles			
Ru(2)–Ru(1)–S(1)	165.22 (8)	Ru(2)–S(3)–C(18)	102.0 (3)
Ru(2)–Ru(1)–O(5)	83.5 (2)	Ru(2)–S(3)–C(21)	106.6 (5)
Ru(2)–Ru(1)–O(7)	83.5 (2)	C(18)–S(3)–C(21)	100.8 (6)
S(1)–Ru(1)–O(5)	85.5 (2)	Ru(4)–S(4)–C(18)	101.7 (4)
S(1)–Ru(1)–O(7)	85.5 (2)	Ru(4)–S(4)–C(22)	105.6 (5)
S(1)–Ru(1)–C(1)	95.2 (4)	C(18)–S(4)–C(22)	100.1 (5)
S(1)–Ru(1)–C(2)	95.3 (4)	Ru(1)–O(5)–C(5)	124.4 (7)
O(5)–Ru(1)–O(7)	84.5 (3)	Ru(2)–O(6)–C(5)	125.3 (7)
Ru(1)–Ru(2)–S(3)	165.74 (7)	Ru(1)–O(7)–C(7)	124.1 (7)
Ru(1)–Ru(2)–O(6)	83.5 (2)	Ru(2)–O(8)–C(7)	122.9 (7)
Ru(1)–Ru(2)–O(8)	84.1 (2)	Ru(3)–O(13)–C(13)	123.9 (7)
S(3)–Ru(2)–O(6)	86.6 (2)	Ru(4)–O(14)–C(13)	121.5 (7)
S(3)–Ru(2)–O(8)	84.8 (2)	Ru(3)–O(15)–C(15)	124.4 (7)
Ru(4)–Ru(3)–S(2)'	167.10 (8)	Ru(4)–O(16)–C(15)	123.8 (7)
O(6)–Ru(2)–C(3)	178.3 (4)	O(5)–C(5)–O(6)	123 (1)
O(6)–Ru(2)–O(8)	83.3 (3)	O(5)–C(5)–C(6)	117 (1)
Ru(4)–Ru(3)–O(13)	83.5 (2)	O(6)–C(5)–C(6)	120 (1)
Ru(4)–Ru(3)–O(15)	83.2 (2)	O(7)–C(7)–O(8)	124 (1)
S(2)–Ru(3)–O(13)	87.5 (2)	O(7)–C(7)–C(8)	119 (1)
S(2)–Ru(3)–O(15)	86.8 (2)	O(8)–C(7)–C(8)	117 (1)
O(13)–Ru(3)–O(15)	84.7 (3)	O(13)–C(13)–O(14)	127 (1)
Ru(3)–Ru(4)–S(4)	165.03 (7)	O(13)–C(13)–C(14)	115 (1)
Ru(3)–Ru(4)–O(14)	84.4 (2)	O(14)–C(13)–C(14)	118 (1)
Ru(3)–Ru(4)–O(16)	83.9 (2)	O(15)–C(15)–O(16)	124 (1)
Ru(1)–S(1)–C(17)	102.7 (4)	O(15)–C(15)–C(16)	118 (1)
Ru(1)–S(1)–C(19)	105.8 (5)	O(16)–C(15)–C(16)	118 (1)
C(17)–S(1)–C(19)	99.0 (6)	S(1)–C(17)–S(2)	111.5 (6)
C(17)–S(2)–C(20)	100.6 (6)	S(3)–C(18)–S(4)	114.3 (6)
Torsion Angles			
O(5)–Ru(1)–Ru(2)–O(6)	–2.3 (3)	O(13)–Ru(3)–Ru(4)–O(14)	–0.4 (4)
O(7)–Ru(1)–Ru(2)–O(8)	–4.1 (3)	O(15)–Ru(3)–Ru(4)–O(16)	–0.2 (3)
C(1)–Ru(1)–Ru(2)–C(3)	–3.4 (6)	C(9)–Ru(3)–Ru(4)–C(12)	–0.1 (7)
C(2)–Ru(1)–Ru(2)–C(4)	–4.9 (5)	C(10)–Ru(3)–Ru(4)–C(11)	1.8 (6)

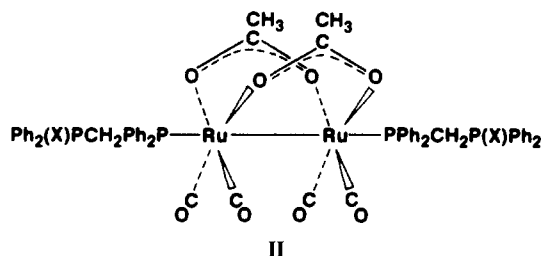
<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits. THF parameters are given in the supplementary material.

determinations gave spurious results, which may indicate a range of molecular masses, and hence it is not possible to define the chain lengths accurately. The resonances observed for the arphos complex (**10**) are accounted for by a random incorporation of the chelate into the polymer chain, which results in chemically inequivalent phosphorus nuclei. Similar observations<sup>16</sup> were made for the osmium analogues  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{L}^-\text{L}^-)]_n$  ( $\text{L}^-\text{L}^- = \text{dppm}, \text{dppe}, \text{arphos}$ ).

The monoselenide of dppm ( $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$ ) reacts rather differently with  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{NCMe})_2]$ , forming the polymer  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2)]_n$  by extrusion of Se, instead of the expected product  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2)]_n$ . Analogous findings in which Se extrusion also occurred have been reported in reactions of  $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$

and  $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$  with other platinum group metals.<sup>17,18</sup>

The reaction of the acetonitrile dimer  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{NCMe})_2]$  with 2 molar equiv of  $\text{Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2$  ( $\text{X} = \text{S}$ , electron pair) in THF results in the quantitative formation of the complexes  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2)_2]$ , which have two dangling diphosphine or diphosphine sulfide ligands bonded in the axial sites opposite the Ru–Ru bond, as shown in species II. The two weakly bound acetonitrile ligands in the



$\text{X} = \text{electron pair (17)}; \text{X} = \text{S (18)}$

starting dimer are replaced by two  $\text{Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2$  ligands, which use only one of their two donor atoms to bond with ruthenium. For the monosulfide complex, coordination occurs via  $\text{PPh}_2$ , rather than sulfur.

The analogous Os(I) complexes  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2)_2]$  ( $\text{X} = \text{S (19)}; \text{X} = \text{electron pair (20)}$ ) were synthesized by heating 2 molar equiv of  $\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$  or  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  with  $[\text{Os}_2(\text{CO})_6(\mu\text{-O}_2\text{CMe})_2]$  under reflux in  $\text{CHCl}_3$  for 2 h. This route is essentially the same as that previously used to prepare the axially substituted complexes  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2\text{L}_2]$ .<sup>6</sup> The coordination of the bidentate ligands in an  $\eta^1$  fashion trans to the Os–Os bond was confirmed in a separate X-ray diffraction study performed on  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$  (**20**).<sup>16</sup> This osmium compound and some related species have recently been reported by Deeming and co-workers.<sup>19</sup>

All of the Ru(I) and Os(I) dimers containing pendant phosphorus ligands exhibit  $^{31}\text{P}\{\text{H}\}$  NMR spectra characteristic of an AA'XX' spin system. Computer simulations of these spectra were successfully completed by using the data given in Table I. As with the Ru(I) polymers, the  $\text{PPh}_2$  groups of the  $\text{Ph}_2\text{PCH}_2\text{P}(\text{X})\text{Ph}_2$  ligands experience a large downfield shift when they are coordinated to the Ru(I) and Os(I) centers. Also, it is worth noting that the  $\eta^1\text{-dppm}$  ligands exhibit larger intraligand  $^{31}\text{P}\text{--C}\text{--}^{31}\text{P}$  couplings than the  $\eta^1\text{-dppmS}$  ligands. We attribute this difference in coupling to a smaller P–C–P angle in the dppm ligands. Furthermore, the  $^{31}\text{P}$  NMR data reveal that there is a significant decrease in the value of  $^3J(\text{P}\text{--M}\text{--M}\text{--P})$  when Ru is exchanged for Os. When  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)_2]$  (**18**) and  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)_2]$  (**19**) are compared, for example, it is found that  $^3J(\text{P}\text{--M}\text{--M}\text{--P})$  drops from 123 to 69 Hz, respectively. This difference probably does not result from geometrical differences in the two complexes, since the covalent radii of Ru and Os are almost identical and analogous structures involving the two metals are found to be virtually superimposable.<sup>12,13,16,20</sup>

The  $^1\text{H}$  NMR data for the species containing pendant phosphines are summarized in the supplementary material along with data for the polymeric complexes. All of the proton NMR data support the  $\eta^1$  formulation. For example, the methylene protons of the  $\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$  ligands in  $[\text{M}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)_2]$ , ( $\text{M} = \text{Ru (18)}; \text{M} = \text{Os (19)}$ ) appear as doublets of virtual triplets, a pattern which could not arise if there were not two magnetically inequivalent, yet chemically equivalent  $\eta^1\text{-dppmS}$  ligands arranged trans to each other across the M–M bond. The IR spectra for all of the dinuclear com-

pounds, which are again characteristic of the sawhorse-type spectra, can also be found in the supplementary material.

The addition of 2 molar equiv of  $\text{H}_2\text{O}_2$  (30% in  $\text{H}_2\text{O}$ ) to  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$  (**20**) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  causes the immediate and quantitative oxidation of the uncoordinated  $\text{PPh}_2$  groups to give  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)_2]$  (**21**). Successful oxidation of the pendant  $\text{PPh}_2$  groups was made apparent by the appearance of a new six-line resonance at 24.23 ppm (half of an AA'XX' spectrum) and the disappearance of the resonance at –27.05 ppm in the  $^{31}\text{P}\{\text{H}\}$  NMR spectrum. The large downfield shift is consistent with a change in the phosphorus oxidation state from III to V.<sup>21,22</sup> Also, the chemical shift for the  $\text{P}(\text{O})\text{Ph}_2$  phosphorus nuclei is quite close to values quoted for the  $\text{P}(\text{O})\text{Ph}_2$  groups of “dangling”  $\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2$  complexes of Pt.<sup>21</sup> Corroborative evidence comes from the IR spectrum, which shows the appearance of a new band at  $1118\text{ cm}^{-1}$ , which has been assigned to the P=O stretch for the phosphorus monoxide moiety.

Polymeric osmium(I) complexes analogous to species **1–10** have been prepared<sup>16</sup> by stirring  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{NCMe})_2]$  with 1 molar equiv of dppm in acetone at room temperature. However, in refluxing THF, only  $[\text{Os}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\eta^1\text{-dppm})_2]$  (**20**) and the unreacted osmium precursor were obtained. Attempts to obtain diruthenium complexes containing two different pendant groups failed. Addition of dppm and dmpm to  $[\text{Ru}_2(\text{CO})_4(\mu\text{-O}_2\text{CMe})_2(\text{RSCH}_2\text{SR})_n]$  resulted in displacement of the dithioether group and formation of the corresponding diphosphine-bridged polymers.

## Conclusions

The products described are not those initially expected on the basis of the normal tendencies of bidentate ligands; so, for example, dppm has an overwhelming tendency to bridge two metals,<sup>23,24</sup> whereas the larger chain length diphosphines ( $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ) tend either to chelate ( $n = 2$ ) or to bridge ( $n > 2$ ).<sup>25</sup> Instead, like monodentate Lewis bases, these groups replace the labile groups in the axial positions of the complexes  $[\text{M}_2(\text{CO})_4(\mu\text{-O}_2\text{CR})_2\text{L}_2]$  ( $\text{M} = \text{Ru, Os}; \text{R} = \text{Me, Et}; \text{L} = \text{NCMe, CO}$ ) and remain in these positions. These diphosphine-containing products, and related species, are inert to ligand rearrangement and to carbonyl loss that would allow the more favored binding modes for the potentially bidentate ligands, so that the expected products are not obtained under the conditions reported. When the above complexes are reacted with diphosphines, diphosphine sulfides, or dithioethers in a 1:1 stoichiometry, these groups bridge the two metals, but not to give discrete binuclear complexes. Instead, unusual polymeric structures result in which these ligands link adjacent “ $\text{Ru}_2$ ” units that have retained the original sawhorse arrangement of carbonyls and carboxylate ligands. In the presence of 2 molar equiv of either dppm or its monosulfide, discrete binuclear species do result; however, the potentially bidentate ligands function as monodentate, pendant groups, again bound in the axial sites of the sawhorse framework.

A forthcoming report and a preliminary communication<sup>2</sup> describe the conditions employed to bring about rearrangement of the core structure of the above polymers and the dimers containing the pendant ligands to give dimeric products in which the more favored bridging and chelating binding modes of diphosphine ligands are obtained.

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(17) Peringer, P.; Schwald, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1625.

(18) Browning, J. University of Victoria, Victoria, British Columbia, Canada. Personal communication.

(19) Deeming, A. J.; Nuel, D.; Randle, N. P.; Whittaker, C. *Polyhedron* **1989**, *8*, 1537.

(20) Bullitt, J. G.; Cotton, F. A. *Inorg. Chim. Acta* **1971**, *5*, 406.

(21) Higgins, S. J.; Shaw, B. L.; Taylor, R. *J. Organomet. Chem.* **1987**, *325*, 285.

(22) Grim, S. O.; Jesson, J. P.; Satek, L. C.; Tolman, C. A. *Inorg. Chem.* **1975**, *14*, 656.

(23) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(24) Puddehatt, R. *J. Chem. Soc. Rev.* **1983**, *12*, 99.

(25) (a) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwan, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347. (b) Balch, A. L.; Tulyathan, B. *Inorg. Chem.* **1977**, *16*, 2840. (c) Sanger, A. R. *J. Chem. Soc., Chem. Commun.* **1975**, 893.

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**Supplementary Material Available:** Tables S1–S7, listing IR and  $^1\text{H}$  NMR data for the compounds, carbon-13 NMR data for complexes

17–21, and anisotropic temperature factors, complete bond angles, calculated hydrogen atom positions, and crystallographic data for compound 11 (15 pages); a table of observed and calculated structure factors for 11 (18 pages). Ordering information is given on any current masthead page.

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## Synthesis and Properties of Binuclear Ruthenium Complexes with 2,7-Bis(2-pyridyl)-1,8-naphthyridine (bnpn). X-ray Crystal Structure of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$

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The compounds  $[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$  (**1**) and  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$  (**2**) have been prepared and characterized. Cyclic voltammetry of **1** in acetonitrile shows two successive one-electron oxidations at 0.64 and 1.34 V (vs SSCE) and two one-electron reductions at  $-0.76$  and  $-1.35$  V. One-electron oxidation of **1** yields the corresponding stable mixed-valence Ru(II)–Ru(III) complex, which has significant metal–metal interactions, as indicated by the electrochemical and spectroscopic data. Complex **2** crystallizes in the tetragonal system, space group  $I4_1cd$ , with  $a = b = 28.659$  (4) Å,  $c = 13.968$  (3) Å, and  $Z = 16$ . The final reliability index  $R$  is 0.076 for 1909 reflections. The Ru–Ru distance is 2.28 (2) Å. The complex is paramagnetic with a  $\mu_{\text{eff}}$  of 2.76  $\mu_B$  at 295 K, corresponding to two unpaired spins. The metal–metal bond order is 2. Cyclic voltammetry of **2** also displays multiple reversible one-electron redox processes at 0.72,  $-0.62$ , and  $-1.37$  V.

### Introduction

Current developments in the area of binuclear ruthenium chemistry have resulted from extensive studies of two important classes of compounds, namely, mixed-valence diruthenium complexes of the Creutz–Taube type<sup>1</sup> and the metal–metal-bonded diruthenium tetracarboxylates and their derivatives.<sup>2,3</sup> In the course of our investigations of the coordination properties of the tetradentate ligand 2,7-bis(2-pyridyl)-1,8-naphthyridine (bnpn), we have found this remarkable ligand forms stable diruthenium complexes that belong to these two distinct classes. The ability of bnpn to support both a multiple metal–metal-bonded and a mixed-valence system is unique with ruthenium; this has not been previously demonstrated in its complexes with copper,<sup>4</sup> rhodium,<sup>5,6</sup> and rhodium.<sup>7</sup> In this article we report the syntheses and characterizations of  $[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$  (**1**) (bpy = 2,2'-bipyridine) and  $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$  (**2**). One-electron oxidation of **1** yields the corresponding mixed-valence complex, the solution properties of which we also describe. Compound **2** is the most stable complex containing the  $\text{Ru}_2^{4+}$  core reported to date; its structure has been determined by X-ray crystallography.

### Experimental Section

**Materials.** Reagent grade chemicals were used without further purification unless otherwise noted. Ruthenium trichloride trihydrate was purchased from Aldrich Chemical Co. The ligand bnpn and  $\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}$  were prepared according to the literature.<sup>8,9</sup> 2,2'-Bipyridine was recrystallized from ethanol prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from ethyl acetate and then dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$ . Sephadex LH-20 was

used as received from Pharmacia Fine Chemicals and regenerated according to standard procedures. Spectrophotometric grade acetonitrile ( $\text{CH}_3\text{CN}$ ), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) utilized in the electrochemical experiments were previously dried over 4-Å molecular sieves. Mallinckrodt spectrAR grade solvents were used for the spectroscopic and conductivity measurements.

**Physical Measurements.** Elemental analyses were performed by Alfred Bernhardt Analytisches Laboratorien. Infrared spectra of samples as KBr pellets were recorded on a Perkin-Elmer 283 or 683 spectrophotometer. Electronic absorption spectra were obtained on Cary 14, 15, and 118 spectrophotometers with 1-cm quartz cells at room temperature.

Molar conductivities,  $\Lambda_m$ , were determined for 1 mM solutions of the complexes in the appropriate solvent by using a Type CDM 2e No. 191500 conductivity meter (The London Co.). Magnetic susceptibility measurements were made by following two procedures: the Evans NMR method<sup>10</sup> and the Faraday method using a Cahn-Ventron Faraday magnetic susceptibility apparatus.

Cyclic voltammetry and controlled-potential electrolysis were performed with an IBM EC/225 voltammetric analyzer. A conventional three-compartment cell was employed with a platinum-ball working electrode, a Pt-wire auxiliary electrode, and an aqueous saturated sodium chloride calomel (SSCE) as reference. A large-area platinum-wire gauze was used in the electrosynthesis experiments. The sample solution was at least 0.5 mM ruthenium complex in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAP and was deaerated with argon prior to each run.  $\Delta E_{1/2}$  values were taken as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the following criteria:<sup>11</sup> (i) the separation between the anodic and cathodic peak potentials ( $\Delta E_p$ ) is  $59/n$  mV, where  $n$  is the number of electrons involved in the redox reaction; (ii) the ratio of the anodic and cathodic peak currents ( $i_{pa}/i_{pc}$ ) is unity.  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  was used as the standard in the electrochemical reversibility experiments. Redox  $n$  values were calculated by using Faraday's law from thin-layer potential-step coulometric data, as described elsewhere.<sup>12</sup>

**Synthesis of Binuclear Complexes.** All reactions were carried out under a nitrogen or argon atmosphere unless indicated otherwise; products were isolated and purified in air.

**$[\text{Ru}_2\text{Cl}_2\text{bnpn}]$ .** (1) To 10 mL of absolute ethanol were added 19.7 mg (75  $\mu\text{mol}$ ) of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 10 mg (35  $\mu\text{mol}$ ) of bnpn. The reaction was instantaneous with immediate formation of a heavy, dark brown

- (1) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1988**, *27*, 364.
- (2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.
- (3) Cotton, F. A.; Matusz, M.; Zhong, B. *Inorg. Chem.* **1988**, *27*, 4368.
- (4) Tikkanen, W. R.; Kruger, K. D.; Bomben, K. D.; Jolly, W. L.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 3633.
- (5) Moya, S. Ph.D. Dissertation, University of California, Santa Barbara, 1981.
- (6) Tikkanen, W. R.; Layman, T. L.; Kane, R.; Moya, S.; Kaska, W. C. *Inorg. Chim. Acta* **1983**, *76*, L29.
- (7) Tikkanen, W. R.; Binamira-Soriaga, E.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 141.
- (8) Caluwe, P. *Macromolecules* **1979**, *12*, 803.
- (9) Stephenson, T. A.; Wilkinson, G. J. *Inorg. Nucl. Chem.* **1966**, *28*, 2285.

- (10) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
- (11) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980; p 228.
- (12) Hubbard, A. T. In *Critical Reviews of Analytical Chemistry*; Meites, L., Ed.; Chemical Rubber Co.: Cleveland, OH, 1973; p 201.