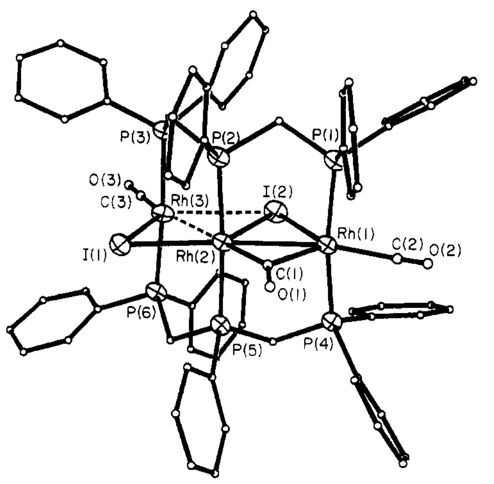


Figure 1. Perspective drawing of [Rh$_3$(μ-dpmp)$_2$(μ-I)$_2$(μ-CO)(CO)]$^+$.

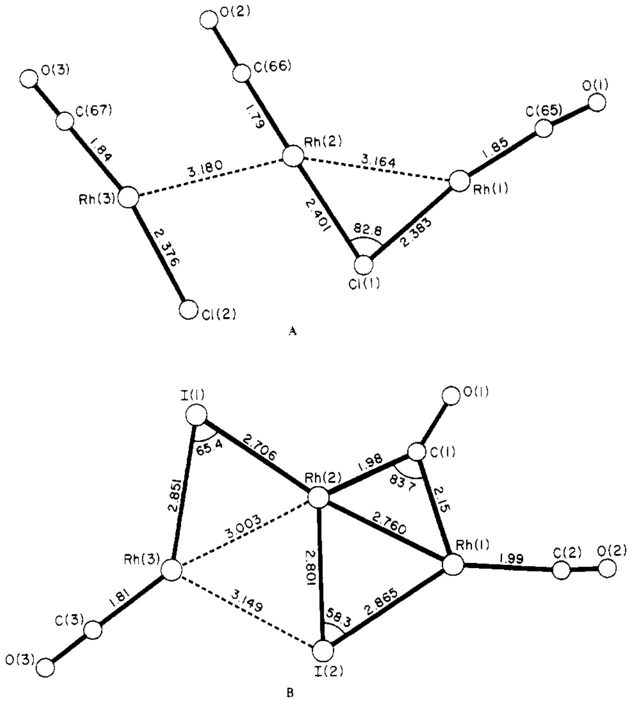
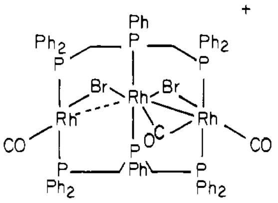


Figure 2. Drawings of planar sections of the structures of [Rh$_3$(μ-dpmp)$_2$(μ-Cl)Cl(CO)$_3$]$^+$ (A) and [Rh$_3$(μ-dpmp)$_2$(μ-I)$_2$(μ-CO)(CO)$_2$]$^+$ (B). For A, esd's are 0.003 Å for Rh–Rh, 0.03 Å for Rh–C, 0.006 Å for Rh–Cl, and 0.2° for Rh–Cl–Rh. For B, esd's are 0.002 Å for bonds involving Rh and I, 0.02 Å for Rh–C, 0.8° for Rh–C–Rh, and 0.1° for Rh–I–Rh; C(2) is disordered, and Rh(1)–C(2) is less accurate.

place of one of the terminal carbonyl groups in **3**, trinuclear **2** has a bridging iodide ligand and Rh(3). Rh(3) is pulled toward Rh(2) and also toward I(2). Although the Rh(3)–I(2) distance is longer than other Rh–I single-bond distances,[6] we still believe that an attractive interaction between these atoms is present and thus I(2) is three-coordinate.

Despite the rather crowded and cramped geometry of **2** (particularly relative to **1**), this molecule is reactive toward the addition of small molecules. For example it (unlike **1**) reacts with carbon monoxide to form a red adduct [Rh$_3$(μ-dpmp)$_2$(CO)$_4$I$_2$][BPh$_4$] with bridging and terminal carbonyl groups (ν(CO) 1980, 1845, 1825, 1775 cm^{-1}).

Metathesis of **1** with sodium bromide yields brown [Rh$_3$(μ-dpmp)$_2$Br$_2$(CO)$_3$][BPh$_4$], which has an infrared spectrum (ν(CO) 1977, 1962, 1813 cm^{-1}) similar to that of **2** and distinct from **1** with only terminal carbonyls. However, its ^{31}P{^{1}H} NMR spectrum is clearly indicative of a fluxional molecule that shows three phosphorus environments at −80 °C (δ_1 23.5, ^1J(P,Rh) = 114.7 Hz, J(P,P) = 25 Hz; δ_2 18.8, ^1J(P,Rh) = 100 Hz, J(P,P) = 50, 25 Hz; δ_3 16.3, ^1J(P,Rh) = 105.9 Hz, J(P,P) = 50 Hz). On warming, the two terminal phosphorus resonances broaden and coalesce so that at 25 °C they are present as a single broad line at 19 ppm. In order to account for this fluxional behavior, we suggest that the bromo compound has a structure similar to that of **2** but with the location of the bridging bromide and carbonyl ligands reversed as shown in **4**. With this structure, movement of the bridging carbonyl serves to render the terminal rhodium and phosphorus environments equivalent. Structure **4** necessarily lacks a counterpart of the Rh(3)–I(1) interaction found in **2**. The smaller size of bromide relative to iodide would require even more compression for the bromo analogue of **2** to exist. Consequently, the size difference between bromide and iodide contributes to the difference in these structures.



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Registry No. **1**, 84774-75-4; **2**, 86372-63-6; **4**, 86365-43-7.

Supplementary Material Available: A list of atomic fractional coordinates and thermal parameters for [Rh$_3$(μ-dpmp)$_2$(μ-I)$_2$(μ-CO)(CO)$_2$][BPh$_4$]·1.28CH$_2$Cl$_2$ (3 pages). Ordering information is given on any current masthead page.

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[6] For comparison, terminal Rh–I units have lengths of 2.735 (1) Å (trans to Rh–Rh) in [(*p*-CH$_3$C$_6$H$_4$NC)$_8$Rh$_2$I$_2$]$^{2+}$ (Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15), 2.761 (1) Å (trans to Rh–Rh) in [(C$_6$H$_5$CH$_2$NC)$_{12}$Rh$_3$I$_2$]$^{3+}$ (Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 3128), and 2.709 (6) Å in [Rh$_6$(CO)$_{15}$I]$^-$ (Albano, V. G.; Bellon, P. L.; Sansoni, M. *J. Chem. Soc. A* **1971**, 678). Bridging Rh–I units have lengths of 2.73 Å (average) in [Rh$_7$(CO)$_{16}$I]$^{2-}$ (Albano, V. G.; Ciani, G.; Martinengo, S.; Chini, P.; Giordano, G. *J. Organomet. Chem.* **1975**, 88, 381) and 3.001 (2) and 2.679 (2) Å in [Rh$_2$(μ-I)$_2$I$_4$(COCH$_3$)$_2$(CO)$_2$]$^{2-}$ (Adamson, G. W.; Daly, J. J.; Forster, D. *Ibid.* **1974**, *71*, C17).

Excited-State Distortions of Tetrakis(μ-trifluoroacetato)dimolybdenum(III)

Sir:

The electronic spectra and structure of binuclear molybdenum complexes containing formal quadrupole bonds are attracting increasing interest.[1-7] A highly resolved vibrational structure has been reported on the 23 000-cm^{-1} $\delta \rightarrow \pi^*$ transition in the title compound.[5] A Franck–Condon analysis

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[1] Dubicki, L.; Martin, R. L. *Aust. J. Chem.* **1969**, *22*, 1571-1587.

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of distortions along normal modes that occur when an excited state is populated can provide direct information about the molecular and electronic structure changes.[8] Only the most intense progression in the $\delta \rightarrow \pi^*$ band has been analyzed.[5] It was interpreted in terms of an elongation of the Mo–Mo bond of 0.1 Å. Recent developments in the time-dependent theory of electronic transitions provide a tool with which both the fine details of the vibronic structure in the absorption spectrum and the normal-mode intensities in the preresonance Raman spectrum can be used to determine the distortions along each normal mode.[9-12] We show here that this theory is applicable to transition-metal complexes by calculating the absorption spectrum from the Raman data. The excited-state distortions of 13 normal modes are determined. The elongation of the Mo–Mo bond is much smaller than expected.

The excited-state distortions and the intensities in the absorption and preresonance Raman spectra are all intimately interrelated. The physical meaning of the relationships is most clearly seen by using the time-dependent theory of spectroscopy.[9] The quantity of interest, $\langle\phi_k|\phi_k(t)\rangle$, is the overlap between the initial packet ϕ_k on the "a" surface and the dynamically evolving packet $\phi_k(t)$ on the "b" surface, where $\phi_k(0) \equiv \phi_k$. The complete overlap for many displaced modes is

$$\langle\phi|\phi(t)\rangle = \exp\left[-\sum_k\left(\frac{{\Delta_k}^2}{2}(1 - e^{-i\omega_k t}) - i\omega_k t/2\right) - iE_0 t/h - \Gamma^2 t^2\right] \tag{1}$$

where E_0 is the electronic energy shift between the minima of the two surfaces a and b and Γ is a Gaussian damping due to relaxation into other modes, the "bath", etc. The absorption cross section at frequency ω is proportional to

$$I(\omega) = \omega\int_{-\infty}^{\infty} e^{i\omega t}\langle\phi|\phi(t)\rangle \, dt \tag{2}$$

Thus, eq 1 for the overlap can be transformed to give the spectrum for a set of ω_k's, Δ_k's, E_0, and Γ.

The Raman cross section is proportional to

$$R(\omega) = \int_{0}^{\infty} e^{i\omega t}\langle\phi_R|\phi(t)\rangle \, dt \tag{3}$$

where the overlap is now between the time-dependent wave packet and the final Raman vibrational state ϕ_R. The half Fourier transform of this overlap gives the Raman spectrum. With the assumption of harmonic oscillator wave functions, no change in normal-mode frequencies, and no Duschinsky rotation, a simple expression relating the intensities I_k and the normal-mode displacements Δ_k has been derived:[12,13]

$$\frac{I_k}{I_{k'}} = \frac{{\Delta_k}^2{\omega_k}^2}{{\Delta_{k'}}^2{\omega_{k'}}^2} \tag{4}$$

The excited-state distortions of the 14 most highly distorted normal modes were calculated from eq 4 and are given in Table I. These distortions were then used in eq 2 to calculate the absorption spectrum. The best fit to the absorption spectrum was produced by slightly varying the distortions around the original values. The final values are given in the table. The calculated spectrum is compared to the published spectrum in Figure 1.

Table I. Distortions and Intensities from the Raman Spectrum and Theoretical Values Used To Calculate the Electronic Absorption Spectrum

Raman values			abs spectrum $\Delta_k/\Delta_{\text{Mo-Mo}}$ [b,c]
freq, cm^{-1}	$I_k/I_{\text{Mo-Mo}}$ [a]	$\Delta_k/\Delta_{\text{Mo-Mo}}$	
263	0.10 ± 0.02	0.43 ± 0.04	0.42
395	1.00 ± 0.00	1.00 ± 0.00	1.00
502	0.84 ± 0.31	0.65 ± 0.11	0.30
515	1.02 ± 0.31	0.69 ± 0.10	0.34
774	0.31 ± 0.08	0.25 ± 0.04	0.21
875	0.14 ± 0.05	0.15 ± 0.03	0.14
1184	0.13 ± 0.03	0.11 ± 0.01	0.09
1212	0.17 ± 0.04	0.12 ± 0.01	0.10
1245	0.16 ± 0.04	0.11 ± 0.02	0.10
1463	2.98 ± 0.69	0.42 ± 0.05	0.28
1486	1.82 ± 0.40	0.32 ± 0.04	0.25
1560	0.15 ± 0.03	0.09 ± 0.01	0.09
1592	0.20 ± 0.05	0.10 ± 0.05	0.10

[a] Calculated by integrating the Raman peaks. [b] ν(Mo–Mo) in the excited state is 355 cm^{-1}.[5] All other frequencies used in the calculation are the Raman-determined values. [c] The values used in eq 1 were $\Gamma = 20$ cm^{-1} and $E_0 = 22\,064$ cm^{-1}; total scaling of distortion is 2.15.

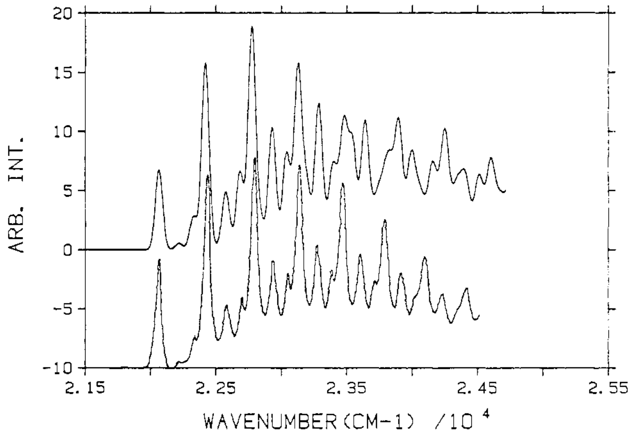

Figure 1. The 23 000-cm^{-1} absorption band: bottom, experimental spectrum (from ref 5); top, calculated spectrum from the Raman-determined distortions given in Table I.

Three aspects of the figure should be noted. First, the electronic spectrum calculated from the Raman data is in excellent agreement with the experimental spectrum through five quanta of vibrational excitation. The fit in the high-energy region is not as good because of anharmonicity, which was not included in eq 4, and/or the presence of a second electronic transition in this region.[2b,5] Second, the displacements that give the best fit to the absorption spectrum are equal to those determined from the Raman spectrum within the experimental uncertainty of the Raman intensity measurements (±20%). Finally, the small peak at 22 217 cm^{-1} cannot be fit by using the Raman data, supporting the interpretation that it arises from a different electronic state.[2b,5,14]

The consistency between the absorption and Raman data provides a new picture of the excited-state distortions. The elongation of the Mo–Mo bond in the excited state is only 0.045 Å, much smaller than the 0.1 Å value, which is obtained on the assumption that only one normal mode is distorted.

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(14) This peak required $\Delta_k/\Delta_{\text{Mo-Mo}} = 0.20$.

Instead, the entire Mo–O–C–O–Mo ring is enlarged.[15] Populating the π^* orbital has only a small effect on the Mo–Mo bond length.

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(15) With a localized-bond stretching model, which neglects coupling to other normal modes, these bond lengthenings are roughly estimated to be Mo–O = 0.03 Å and O–C = 0.006 Å.

Articles

Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557, and University of Hawaii at Manoa, Honolulu, Hawaii 96822, and Equipe CNRS/SNPE, 94320 Thiais, France

Ruthenium(II) Complexes of 1-Substituted 3,4-Dimethylphospholes

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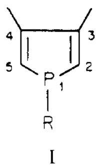
Several ruthenium(II) complexes of 1-substituted 3,4-dimethylphospholes, (RDMP, R = CH_3, n-C_4H_9, t-C_4H_9, C_6H_5, and $C_6H_5CH_2$) have been prepared and characterized by elemental analyses and infrared and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Stable carbonyl complexes of the types *cis*- and *trans*-$Ru(CO)_2(RDMP)_2Cl_2$ and one example of $(RDMP)_3Ru(CO)Cl_2$ (R = C_6H_5) were prepared. In each case, the kinetically formed *trans*-$(RDMP)_2Ru(CO)_2Cl_2$ thermally isomerizes smoothly to the thermodynamically stable *cis*-$(RDMP)_2Ru(CO)_2Cl_2$. These phospholes are shown to be better donors than PPh_3 toward ruthenium(II) as they readily displace PPh_3 from $(PPh_3)_4RuCl_2$ in refluxing hexane to produce *cis*- and *trans*-$(RDMP)_4RuCl_2$ (R = CH_3, n-C_4H_9, C_6H_5, and $C_6H_5CH_2$) in moderate yield. With the sterically more bulky 1-t-C_4H_9DMP, the pentacoordinate (t-BuDMP)$_2$(PPh_3)$RuCl_2$ is obtained under these same conditions. The kinetically formed *trans*-$(RDMP)_4RuCl_2$ complexes only slowly dissociate in solution and undergo both thermal and photochemical isomerization to the thermodynamically stable *cis*-$(RDMP)_4RuCl_2$ with some attendant decomposition. The pentacoordinate (t-BuDMP)$_2$(PPh_3)$RuCl_2$ is much more dissociately stable than $(PPh_3)_3RuCl_2$ and displays phosphorus–phosphorus coupling at room temperature whereas, for $(PPh_3)_3RuCl_2$, this coupling is not observable above −90 °C in CH_2Cl_2 solutions. The crystal structure of $(PhDMP)_3Ru(CO)Cl_2$ has been determined by three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions a = 13.789 (2) Å, b = 14.752 (3) Å, c = 9.915 (2) Å, α = 98.37 (1)°, β = 111.80 (1)°, γ = 95.08 (1)°, ρ_{calcd} = 1.39 g cm^{-3}, and ρ_{obsd} = 1.40 (5) g cm^{-3} with Z = 2. Refinement converged to R = 0.039 with 4235 independent reflections. Within this molecule, there exist interesting charge-transfer type interactions which seemingly stabilize one particular isomeric configuration. Some of these complexes have been shown to catalyze the hydrogenation of 1-heptene at ambient temperature and pressure at rates comparable to this same catalysis by $(Ph_3P)_3RuCl_2$.

Introduction

In the last decade, considerable interest has been focused on the chemistry of phospholes.[2] Phospholes (I) are structurally similar to the aromatic pyrroles but debate continues as to whether phospholes are aromatic.[2] Evidence supporting some degree of cyclic conjugation in phospholes is based upon[3] complexation experiments and pK_a values, the low rates of quaternization[4] of various phospholes, low phosphorus inversion barriers in phospholes,[5] comparative bond lengths of phospholes and phosphines,[6a] low bond energies of the P=O bond[6b] in some phosphole oxides, and theoretical studies.[7] Overall, these studies indicate that unsubstituted phospholes have limited basicity, are sterically compact, and exhibit variable amounts of delocalization of the phosphorus lone pair. Ring substitution by methyl groups increases the phosphorus donor ability considerably such that stable complexes of the type $(RDMP)_2PdX_2$[8] and $(RDMP)_2PtX_2$[9] are easily formed.



I

structure and ring-numbering scheme of 1-R-3,4-dimethylphospholes

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(1) (a) University of Nevada. (b) University of Hawaii. (c) Equipe CNRS/SNPE.

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