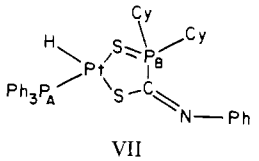

VII

shows a platinum–hydrogen stretch at 2154 cm^{-1}, a strong band at 1540 cm^{-1} assigned to the CN stretch, and a P–S stretch at 602 cm^{-1} (622 cm^{-1} for the free ligand). All these data together with the NMR data (Table V) are consistent with the proposed structure VII.

Conclusions

We have compared the reactions of a range of ligands of the types $R_2P(S)C(S)SR'$, $R_2PC(S)NPhH$, and $R_2P(S)C(S)NPhH$ with $(PPh_3)_2PtC_2H_4$. $R_2P(S)C(S)SR'$ ligands form stable η^2-CS-bonded complexes in a manner similar to that previously reported[2] for $Ph_3SnC(S)SR'$ ligands. None of the complexes with these types of ligands show any tendency to internally rearrange through oxidative addition. In contrast, the thioformamide ligands $Ph_3SnC(S)NPh$,[2] $R_2PC(S)NPhH$, and $R_2P(S)C(S)NPhH$ give η^2-CS-bonded complexes, which in general do undergo internal oxidative additions of various types. For the phosphorus-based ligands, the rate of reaction of the initially formed η^2-CS compound appears to depend upon the base strength of the phosphorus portion of the ligand, reactivity decreasing in the sequence $Cy_2P \gg Ph_2P > Cy_2P(S) \gg Ph_2P(S)$. In all cases, hydride transfer to platinum is the last step in the reaction.

Acknowledgment. S.W.C. thanks the Commonwealth Government for a Commonwealth Postgraduate Research Award.

Registry No. 1 (R = Ph), 88548-34-9; **1** (R = Cy), 88548-37-2; II (R = Ph, R' = Me), 88548-30-5; II (R = Ph, R' = CH_2Ph, 88548-31-6; II (R = Cy, R' = Me), 88548-32-7; II (R = Cy, R' = CH_2Ph), 88548-33-8; V, 88548-39-4; VI, 88548-40-7; VII, 88548-41-8; **3** (R = Cy), 88548-38-3; $(PPh_3)_2Pt(Ph_2PC(S)NPh(SiMe_3))$ (η^2-CS-bonded isomer), 88548-35-0; $(PPh_3)_2Pt(Ph_2PC(S)NPh(SiMe_3))$ (P,S-bonded isomer), 88548-36-1; $(PPh_3)_2PtC_2H_4$, 12120-15-9; $(PPh_3)_4Pt$, 14221-02-4; $Ph_2PC(S)NPhH$, 739-61-7; $Cy_2PC(S)NPhH$, 899-27-4; $Ph_2P(S)C(S)SMe$, 28658-59-5; $Cy_2P(S)C(S)SMe$, 88525-71-7; $Ph_2P(S)C(S)SCH_2Ph$, 28658-61-9; $Cy_2P(S)C(S)SCH_2Ph$, 88525-72-8; $Ph_2P(S)C(S)NPhH$, 7067-81-4; $Cy_2P(S)C(S)NPhH$, 14633-83-1; $Ph_2PC(S)NPh(SiMe_3)$, 18789-75-8; sulfur, 7704-34-9.

Contribution from Central Research—New England Laboratory, Dow Chemical USA, Wayland, Massachusetts 01778, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Reexamination of the Reactions of $Ph_2P(CH_2)_nPPh_2$ (n = 1–4) with $RuCl_2(PPh_3)_3$

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Received June 2, 1983

A reinvestigation of the reaction of $RuCl_2(PPh_3)_3$ with the chelating diphosphines $Ph_2P(CH_2)_nPPh_2$, n = 1–4, reveals chemistry very dependent on the length of the methylene chain. Only for n = 4 is the complex $RuCl_2(PPh_3)$(chelate) isolatable. ^{31}P NMR studies reveal numerous halo-bridged species in solution for the various ligands. Neither dppe nor dppm forms coordinatively unsaturated $RuCl_2(PPh_3)$(chelate), which is explained as a function of the chelate bite angle.

Our recent studies on the dehydrogenation of alcohols[1] and amines[2] using Ru(II) phosphine catalysts led us to prepare several Ru(II) complexes containing the bidentate phosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp; n = 4, dppb). Others[3] have noted that the addition of 2 equiv of $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) to a suspension of $RuCl_2L_3$ (L = PPh_3) gives yellow complexes of composition $RuCl_2[Ph_2P(CH_2)_nPPh_2]_2$. Such complexes were shown to have octahedral stereochemistry with trans chloride ligands. When n = 4, however, it has been reported[4] that an insoluble, dimeric, light green complex analyzing as $[RuCl_2(dppb)_{1.5}]_2$ results. We have conducted detailed studies on such reactions using $^{31}P\{^1H\}$ NMR in hope of determining the optimum conditions for the isolation of species of the type $RuCl_2PPh_3(Ph_2P(CH_2)_nPPh_2)$, and herein we report these studies.

Experimental Section

Unless indicated otherwise, all operations were conducted under purified argon or nitrogen by using standard inert-atmosphere techniques. NMR spectra were recorded on JEOL FX90-Q and Varian XL-100 spectrometers. Phosphorus-31 chemical shifts were referenced to external H_3PO_4, positive chemical shifts being downfield of this reference. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

The diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1–4) were obtained from Strem Chemical, Inc., and were used without further purification. Solvents were reagent grade, dried with 3-Å molecular sieves, and deoxygenated with bubbling argon or under vacuum prior to use. Literature methods and modifications of these (see below) were used to prepare $RuCl_2(Ph_2P(CH_2)_nPPh_2)_2$ (n = 1–3)[3] and $[RuCl_2(Ph_2P(CH_2)_4PPh_2)_{1.5}]$.[4]

$RuCl_2$(chelate)$_2$. *trans*-$RuCl_2(dppe)_2$ and *trans*-$RuCl_2(dppm)_2$ were prepared from $RuCl_3 \cdot 3H_2O$ and the bidentate phosphine (mole ratio 1:2.5) by reflux in ethanol.[5,6] The absence of the cis isomer in the precipitated product was established by ^{31}P NMR. The analogous reaction (2-h reflux in methanol) was carried out for dppp, but product isolation was carried out by removal of methanol under vacuum followed by dissolving the solid residue in CH_2Cl_2. This solution was sealed under vacuum in an NMR tube. The ^{31}P NMR spectrum of this solution showed (in addition to dppp and its monoxide) *cis*- and *trans*-$RuCl_2(dppp)_2$ in a 2:1 mole ratio. ^{31}P NMR parameters of *cis*-$RuCl_2(dppp)_2$ (in CH_2Cl_2 at 303 K) are as follows: 42.0 (t), −2.7 ppm (t, J = 31.5 Hz).

Preparation of $RuCl_2(PPh_3)(Ph_2P(CH_2)_4PPh_2)$. $RuCl_2(PPh_3)_3$ (1.004 g, 1.047 mmol) and dppb (0.449 g, 1.053 mmol) were mixed together in a Schlenk tube under argon in 50 mL of CH_2Cl_2. A bright green material began to precipitate immediately. The suspension was stirred an additional 0.5 h and then transferred by cannula to 150 mL of dry degassed ethanol to precipitate the remaining Ru complexes and remove PPh_3. The precipitate was filtered, washed with 100 mL of ethanol and 100 mL of petroleum ether, and vacuum dried;[7] yield

† Dow Chemical Co.
‡ Indiana University.

(1) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.
(2) Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042.
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(4) Bressan, M.; Rigo, P. *Inorg. Chem.* **1975**, *14*, 2286.
(5) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.
(6) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1972**, *11*, 2714.

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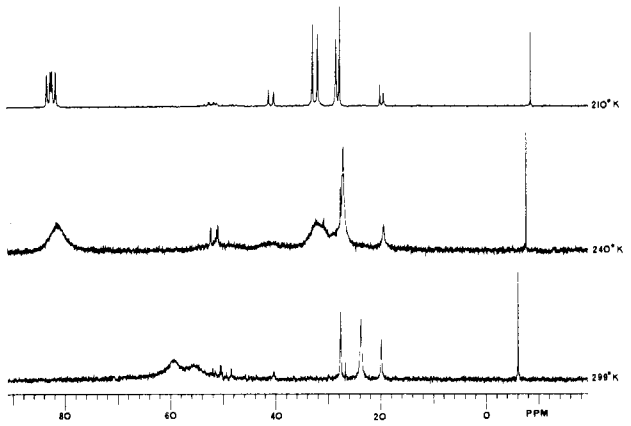


Figure 1. $^{31}P\{^1H\}$ NMR spectra of $RuCl_2PPh_3[Ph_2P(CH_2)_4PPh_2]$ (0.053 M in CD_2Cl_2, 36.45 MHz).

Table I. ^{31}P NMR Parameters[a,b] for $RuCl_2(PPh_3)$(chelate)

	δ_A	δ_B	δ_X	J_{AB}	J_{BX}	J_{BX}
dppb	26.3	35.2	83.2	302.4	−22.6	−37.5
dppp	19.6	34.3	72.9	299.1	−20.6	−53.3

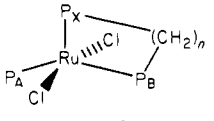
[a] In CH_2Cl_2 at 198 K. [b] From only the static spectrum, the relative signs of J_{AX} and J_{BX} are known, but nothing can be determined about the sign of J_{AB} relative to these. This statement applies individually to each of the solutions presented here.

0.60 g (66%). Anal. Calcd for $RuCl_2PPh_3(Ph_2P(CH_2)_4PPh_2)$: Ru, 11.75; Cl, 8.24; P, 10.80. Found: Ru, 11.29; Cl, 8.58; P, 10.76.

Reactions of $RuCl_2(PPh_3)_3$ with Equimolar dppm, dppe, and dppp. The phosphine chelate (0.1 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of 0.1 mmol of $RuCl_2(PPh_3)_3$ in 10 mL of CH_2Cl_2. The resultant solution was stirred at room temperature for 1 h and then concentrated to approximately 5 mL. A portion of this solution was loaded directly into an NMR tube and then sealed under vacuum.

Results and Discussion

$RuCl_2(PPh_3)$(dppb). The reaction of 1 equiv of dppb with $RuCl_2(PPh_3)_3$ in CH_2Cl_2 produced a green complex of stoichiometry $RuCl_2(PPh_3)$(dppb) (I). The $^{31}P\{^1H\}$ NMR



I, $n = 3, 4$

spectrum of this complex (0.053 M) in CD_2Cl_2 was highly temperature dependent (Figure 1). The major species in solution exhibit an AB_2 splitting pattern above ca. 315 K and an ABX pattern below 210 K (Table I). All spectra also show some PPh_3. The spectral parameters of the ABX pattern are characteristic of two *cis*- and one *trans*-phosphorus–phosphorus interaction. With selective decoupling of the phenyl protons, the line widths of the highest field resonance (A) remained narrow, while the two lower field resonances (B and X) were broadened by unresolved coupling to the dppb methylene protons. The highest field chemical shift (δ_A) is also close to that of the basal PPh_3 in $RuCl_2(PPh_3)_3$ (24.1 ppm). These data are consistent with a five-coordinate structure (I) similar to that of $RuCl_2(PPh_3)_3$. A detailed line-shape analysis of the $^{31}P\{^1H\}$ NMR spectra of the analogous complex $RuCl_2(PPh_3)$(dppp) (vide infra) indicates that this dynamic NMR behavior is due to intramolecular exchange of the B and X nuclei.

(7) Occasionally, small quantities of $[RuCl_2(dppb)_{1.5}]_2$ are present in the precipitate. It can be removed simply by dissolving the $RuCl_2PPh_3$(dppb) in CH_2Cl_2 and leaving the impurity behind.

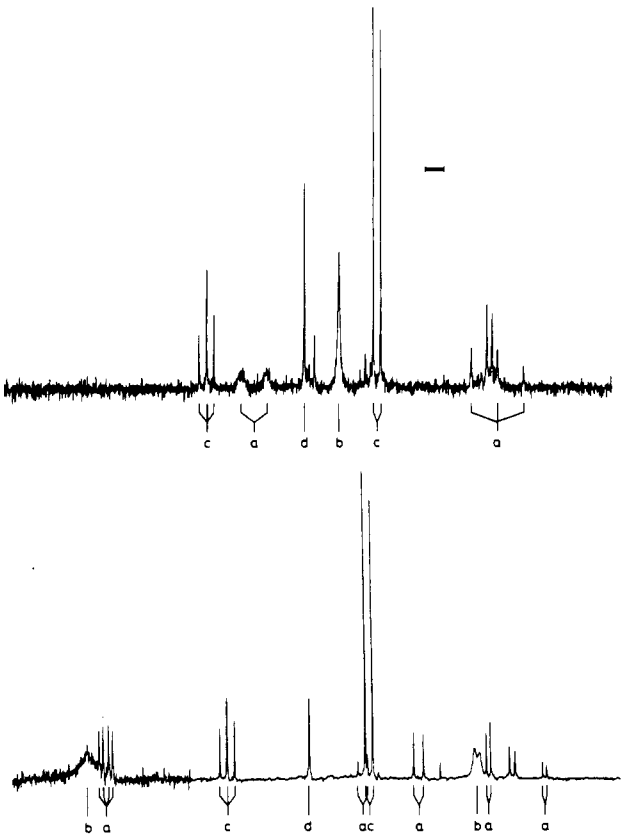
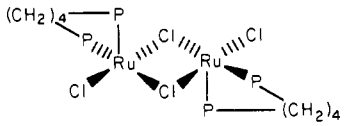


Figure 2. 40.5-MHz $^{31}P\{^1H\}$ NMR spectra of the products of reaction of $RuCl_2(PPh_3)_3$ and dppp in CH_2Cl_2 at 303 K (top) and 198 K (bottom). The region from 5 to 84 ppm is shown; the amplitude at the left end of the 198 K spectrum has been doubled. The calibration bar indicates 100 Hz. Peaks marked a are due to $RuCl_2(PPh_3)$(dppp), and those marked b are due to $RuCl_2(PPh_3)_3$. The singlet due to *trans*-$RuCl_2(dppp)_2$ is outside of the spectral region displayed, as is that of PPh_3.

At 210 K, free PPh_3 is still present, as well as an AB quartet ($\delta_A = 62.6$, $\delta_B = 54.4$ ppm; $J_{AB} = 47$ Hz).[8] Comparison to the solution dynamics[9] of $RuCl_2(PPh_3)_3$ suggests that a structure such as II is responsible for the AB multiplet. Under



II

these conditions (0.053 M Ru, 210 K), the degree of dissociation of $RuCl_2(PPh_3)$(dppb) to PPh_3 and II is roughly 9%. The rate of this dissociation is much slower than the rate of intramolecular site exchange of I (the PPh_3 line width is essentially invariant over the temperature range 315–210 K).

The ^{31}P NMR spectrum of I after addition of further dppb reveals only the above ABX and AB multiplets. Examination of the NMR tube reveals a green microcrystalline material has precipitated that analyzes as $[RuCl_2(dppb)_{1.5}]_2$, as previously described.[4] This material is insoluble in all common organic solvents precluding NMR examination and stereochemical assignment.[10]

Reaction of $RuCl_2(PPh_3)_3$ with $Ph_2P(CH_2)_3PPh_2$(dppp). The ^{31}P NMR spectrum of the products of the reaction of 0.1 mmol of $RuCl_2L_3$ and 0.1 mmol of dppp in 5 mL of CH_2Cl_2

(8) These parameters were obtained from spectra where a higher concentration of this species allowed us to accurately fit the AB pattern.
(9) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.
(10) We are attempting to grow X-ray-quality crystals of this complex in order to elucidate its structure.

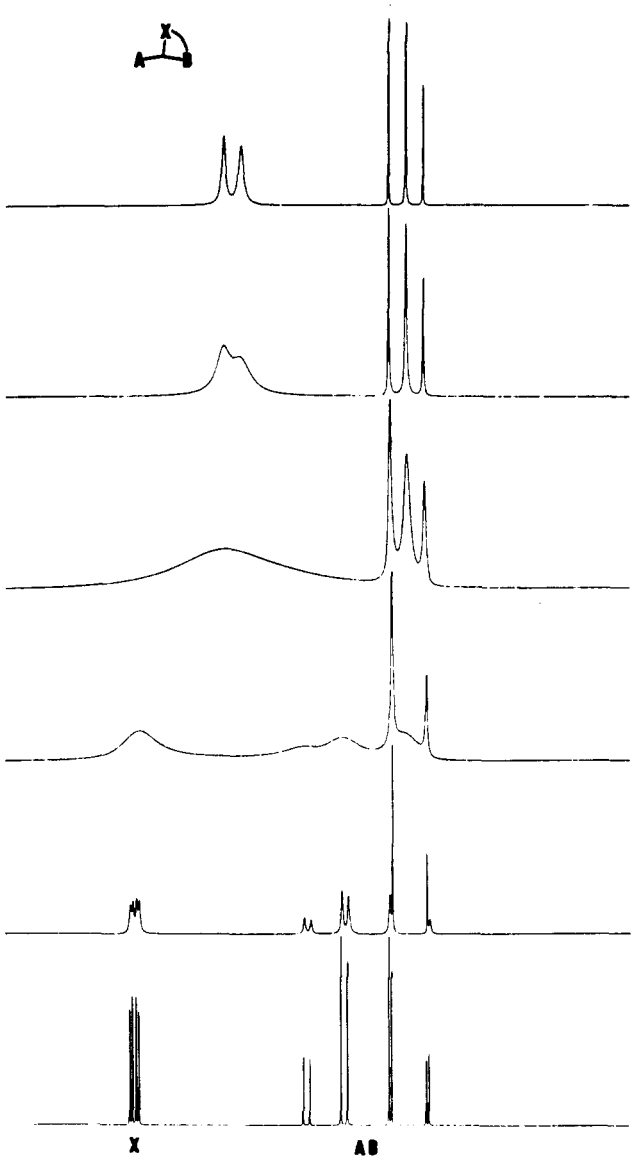
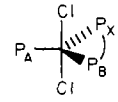


Figure 3. Simulation of B,X exchange in the ^{31}P NMR of $RuCl_2(PPh_3)(dppp)$.

contains numerous resonances and is also temperature dependent (Figure 2). At 303 K one can easily assign resonances due to PPh_3, $RuCl_2L_3$, and *trans*-$RuCl_2(dppp)_2$. The last assignment was made by independent synthesis. At 198 K four patterns are evident: an ABX pattern (a), $RuCl_2L_3$ (b), an AX_2 pattern (c), and a singlet (d). There are no resonances indicative of monodentate dppp.

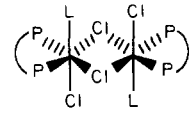
The ABX pattern has spectral parameters shown in Table I. The spectrum varies with temperature (Figure 2). Immediately evident is the known[9] dynamic behavior of $RuCl_2L_3$ (pattern b), which changes from an AX_2 pattern at 198 K to a singlet at 303 K. Pattern c exhibits somewhat temperature-dependent chemical shifts but not dynamic behavior. The ABX pattern (a) is strongly temperature dependent in a manner analogous to that of I. This behavior can be simulated on the assumption that only the B and X nuclei undergo exchange. The 303 K pattern approximates an AB_2 pattern. A series of calculated spectra are displayed in Figure 3. In the fast-exchange limit (303 K) the line spacing is the average of the static values of J_{AB} and J_{AX}. The observed value (140 Hz) is consistent with the parameters of Table I, with J_{AB} opposite in sign to J_{BX} and J_{AX}. The nonrigidity of this ABX spin system implies a five-coordinate species, I, analogous to $RuCl_2L_3$ and $RuCl_2L(dppb)$. The extreme low-field position for the X nucleus identified it as the apical phosphorus (compare $RuCl_2L_3$). This is significant, since major angular distortions of the first coordination sphere (normal apical-to-basal angle of 104°) are required when dppp (intrachelate P–M–P angle ~93°) connects apical and basal sites.[11] Clearly, the chelate can never span trans-basal positions in I, and the intramolecular rearrangement must therefore pass through a "pinched" trigonal bipyramid (III) in order to move



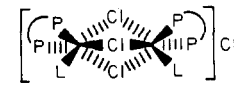
III

P_X to a basal position. If S^* is taken to be zero (compare $RuCl_2L_3$),[9] the rate constant at 303 K yields a value of ΔH^* of 11.0 ± 0.2 kcal/mol. The angular compression ($\angle P_X$–Ru–P_B) in the transition state III thus raises ΔH^* 1 kcal/mol over that found for $RuCl_2L_3$.

The AX_2 pattern (c) cannot be unequivocally assigned to a specific compound, but some structural deductions can be made. The magnitude of the coupling constant (39.7 Hz) implies A is cis to both X nuclei. The X resonance is abnormally intense (A:X ratio ~1:3), suggesting an increased Overhauser effect at the X nuclei. This suggests the X nuclei may be coordinated dppp, since the ligand has methylene protons absent on PPh_3. The molecule is stereochemically rigid, suggesting six-coordination. Structures IV and V are consistent with these features.



IV

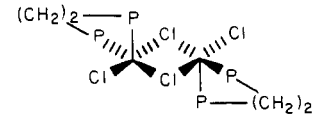


V

The singlet (d) remains unassigned.

This reaction of $RuCl_2L_3$ with dppp is curiously stereospecific in one regard. Of the two possible isomers of $RuCl_2(dppp)_2$, only the trans species is produced. Direct reaction of $RuCl_3 \cdot 3H_2O$ with dppp produces cis in preference to trans by a 2:1 ratio.

Reaction of $RuCl_2(PPh_3)_3$ with $Ph_2P(CH_2)_2PPh_2$(dppe). Reaction of equimolar amounts of $RuCl_2L_3$ and dppe produced *trans*-$RuCl_2(dppe)_2$ (verified by independent synthesis) as *one* major product. Free PPh_3 and unreacted $RuCl_2L_3$ are also evident. Significantly (in contrast to the situation with dppm, see below), $RuCl_2L_3$ is present in only minor amounts in spite of a reaction stoichiometry that might require recovery of 50% of the $RuCl_2L_3$ initially supplied. The consumption of unexpected quantities of $RuCl_2L_3$ is related to the formation of two additional products. One, of intensity equal to that of *trans*-$RuCl_2(dppe)_2$, exhibits an AB spectral pattern with (195 K) $\delta_A = 76.6$, $\delta_B = 73.3$, and $J_{AB} = 30.5$ Hz. This is consistent with structure VI, the analogue of II. When the temperature



VI

is raised, to 303 K, δ_A and δ_B change to 76.8 to 76.0, so as to markedly alter the appearance of the spectrum. However, this molecule, like $Ru_2Cl_2(PPh_3)_4$,[9] is not fluxional. The second product, of approximately one-third the intensity of VI, shows an ABX pattern ($\delta_A = 60.9$, $\delta_B = 58.4$, $\delta_X = 42.2$; $J_{AB} = 19$, $J_{AX} = 31$, $J_{BX} = 32$ Hz). This species cannot be $RuCl_2(PPh_3)(dppe)$ since it is stereochemically rigid at 303 K and

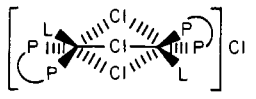
(11) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973**, *12*, 531.

Table II. ^{31}P NMR Parameters

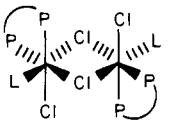
	chem shift[a]	coord chem shift[b]
trans-$RuCl_2(dppm)_2$	−7.7	15.9
trans-$RuCl_2(dppe)_2$	44.3	56.8
trans-$RuCl_2(dppp)_2$	−5.0	12.3
cis-$RuCl_2(dppp)_2$	42.0, −2.7 (J = 31.5 Hz)	59.3, 14.6

[a] In CH_2Cl_2 at 303 K. [b] δ[$RuCl_2$(chelate)$_2$] − δ(chelate).

all J values indicate cis stereochemistry. Two structures consistent with these facts are shown as VII and VIII.



VII



VIII

Reaction of $RuCl_2L_3$ with $Ph_2PCH_2PPh_2$ (dppm). Reaction of equimolar amounts of $RuCl_2L_3$ and dppm produces *trans*-$RuCl_2(dppm)_2$ as the major product. Again, free PPh_3 and unreacted $RuCl_2L_3$ are evident, but free and monodentate dppm are absent. No ABX pattern is observed (i.e., $RuCl_2(PPh_3)$(dppm) is not produced), nor are there any other singlet resonances. A 6% yield of an AB pattern consistent with VI is also observed.

Conclusion

The $^{31}P\{^1H\}$ NMR spectra of these $RuCl_2(Ph_2P(CH_2)_nPPh_2)_2$ complexes (Table II) warrant no further discussion other than their adherence to the ΔR rule,[12] which notes that phosphorus ligands involved in chelate rings reveal coordination chemical shifts (Δ) outside the range normally predicted by the $\alpha = A\delta F + B$ relationship.[13] In qualitative terms, one observes that, compared to a nonchelated, cis-disubstituted analogue, four-membered rings are shielded more than six-membered rings and five-membered rings are deshielded. This trend is also evident in comparing VI (dppe) with II (dppb). The large downfield shift for phosphorus trans to chlorine in *cis*-$RuCl_2(dppp)_2$ is noteworthy. The same effect is evident in isoelectronic *cis*-$IrCl_2(dppe)_2^+$.[14]

Neither dppe or dppm forms coordinatively unsaturated $RuCl_2(PPh_3)$(chelate). This is presumably a function of chelate bite angle. As this angle becomes smaller, the coordination sphere about ruthenium becomes less sterically congested and $RuCl_2(PPh_3)$(chelate), once formed, is accessible to further reaction to form coordinatively saturated monomeric or dimeric products.

Acknowledgment. We gratefully acknowlege support of this work by the Research Corp. and the National Science Foundation (Grant GP-38641X).

Registry No. I, 88496-72-4; II, 88496-73-5; $[RuCl_2(dppb)_{1.5}]_2$, 55669-36-8; *trans*-$RuCl_2(dppp)_2$, 55669-28-8; *trans*-$RuCl_2(dppe)_2$, 19349-72-5; *trans*-$RuCl_2(dppm)_2$, 38800-82-7; $RuCl_2(PPh_3)_3$, 15529-49-4.

(12) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.
(13) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 1104.
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Oxo-Bridged Mixed-Oxidation-State Complexes of Molybdenum: Preparation, Properties, and X-ray Structure of $[Mo_2O(S_2CNEt_2)_6]BF_4$ and Related Compounds

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The oxo-bridged mixed-oxidation-state compound $[Mo_2O(S_2CNEt_2)_6]BF_4$ has been prepared by the reaction of $[MoO(S_2CNEt_2)_3]BF_4$ and triphenylphosphine and fully characterized by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $C2/c$ with a = 13.24 (1) Å, b = 30.86 (4) Å, c = 12.42 (1) Å, β = 97.89 (4)°, and Z = 4. The structure was refined by full-matrix least-squares methods to final residual values of R = 0.035 and R_w = 0.041 on the basis of 3131 independent reflections. The cation contains two pentagonal-bipyramidal (asymmetric) units linked by an almost linear (Mo–O–Mo = 175.6 (2)°) bridging oxo ligand having Mo–O bond lengths of 1.848 (2) Å. It is the first dithiocarbamato complex of molybdenum to exhibit oxo bridging in the absence of terminal oxo ligands and is the first dinuclear seven-coordinate molybdenum complex in which an axial oxygen atom functions as the bridging group. The compound is paramagnetic (μ_{eff} = 2.17 μ_B), is a 1:1 electrolyte in methanol, and shows an intervalence-transfer band at 1310 nm ($\epsilon \approx$ 1100 L cm^{-1} mol^{-1}). The detailed crystal and molecular structure, electrochemistry, and spectral characteristics of the compound are presented and discussed as is the nature of the mixed oxidation state. The preparation and properties of the analogous dimethyldithiocarbamato complex and of the PF_6^-, ClO_4^-, and Cl^- salts of both complexes are also described.

Introduction

Dinuclear molybdenum centers have been postulated for xanthine oxidase, sulfite oxidase, and nitrate reductase, and their participation in the catalytic cycles of these enzymes has been suggested.[2] For a dinuclear active-site model, the mononuclear Mo(V) characteristics of the enzyme ESR signals[3,4] may be understood in terms of mixed-oxidation-state centers [Mo(IV, V) or Mo(V, VI)] in which the unpaired electron is localized on only one molybdenum atom. In terms of enzyme model studies, however, there is a notable lack of simple complexes that adequately model these mixed-oxidation-state centers. At present, the majority of mixed-oxidation-state

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