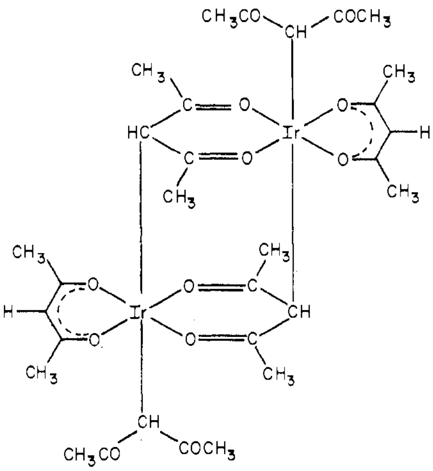

II

sumably arising from the bridging acac group, in addition to bands characteristic of O-bonded bidentate and γ-C-bonded acac groups (Table I). Gibson[11] reported that $[(CH_3)_3Pt(acac)]_2$ shows its $\nu(C{=}O)$ band at 1600 cm^{-1}, although other complexes believed to contain bridging acac groups, such as $[Rh(acac)(C_2F_4)(CH_3CN)]_2$ and $Co[PtCl(acac)_2]_2$, absorb in the 1640–1660-cm^{-1} region. Compound **5** is the first example of a complex which contains three different types of coordinated acac.

Attempts to convert O-bonded bidentate acac into γ-C-bonded acac on iridium(III) have not been successful; e.g., **1** is recovered almost quantitatively after heating in pyridine for 4 h, and there is no evidence for the formation of **3**. This is in marked contrast with the behavior of Pd^{II}–acac complexes; e.g., $Pd(acac)_2$, containing bidentate O-bonded acac, is converted almost quantitatively into $Pd(O\text{-acac})[CH(COCH_3)_2]py$ by treatment with pyridine at 80 °C.[2] The difference is undoubtedly due to the presence of a vacant coordination site on palladium(II), so that pyridine or other ligands can promote the change from O to C bonding. The reverse change does occur to a limited extent on iridium(III), since attempted sublimation of **5** at 270 °C (0.2 mm) gave an approximately 10% yield of **1**, in addition to unidentified decomposition products.

The low yield of $Ir(O\text{-acac})_3$ in this and previous preparations is due, at least in part, to the simultaneous formation of γ-C-bonded complexes. Iridium(III) clearly resembles isoelectronic platinum(IV) in binding strongly to the γ-carbon atom of 2,4-pentanedione to give octahedrally coordinated complexes.

Registry No. 1, 15635-87-7; **3**, 60195-60-0; **4**, 60209-65-6; **5**, 60184-33-0; **6**, 60195-61-1; **7**, 60195-62-2.

References and Notes

(1) D. Gibson, *Coord. Chem. Rev.*, **4**, 225 (1969), and references cited therein.
(2) S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 665 (1974).
(3) See ref 1, p 230.
(4) Abbreviations: acac = 2,4-pentanedionato (acetylacetonato), $[CH_3COCHCOCH_3]^-$; py = pyridine; *n*-Pr = *n*-propyl.
(5) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953).
(6) J. G. Gordon, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, **5**, 381 (1971).
(7) This designation ignores coupling with C$\cdots$C stretching modes; see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley-Interscience, New York, N.Y., 1970, p 248.
(8) A. G. Swallow and M. R. Truter, *Proc. R. Soc. London, Ser. A*, **254**, 205 (1960).
(9) G. Ingrosso, A. Immirzi, and L. Porri, *J. Organomet. Chem.*, **60**, C35 (1973).
(10) G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, **87**, 5356 (1965).
(11) See ref 1, p 233.

Contribution from the Research School of Chemistry,
Australian National University, Canberra, Australia 2600

Ground-State Geometries and Fluxional Behavior of Octakis(trifluorophosphine)dirhodium, Octakis(trifluorophosphine)diiridium, and Related Trifluorophosphine Complexes

M. A. Bennett,* R. N. Johnson, and T. W. Turney

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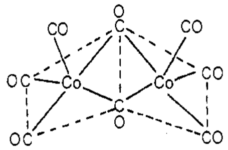
The reactions of dirhodium octakis(trifluorophosphine), $Rh_2(PF_3)_8$,[1,2] with hydrogen[2], group 4 hydrides[2], and acetylenes[3] (eq 1–3) are remarkably similar to the corresponding reactions of dicobalt octacarbonyl, $Co_2(CO)_8$.

$$Rh_2(PF_3)_8 + H_2 \rightarrow 2HRh(PF_3)_4 \quad (1)$$

$$Rh_2(PF_3)_8 + (C_6H_5)_3MH \rightarrow HRh(PF_3)_4 + (C_6H_5)_3MRh(PF_3)_4 \quad (2)$$
(M = Si or Ge)

$$Rh_2(PF_3)_8 + \text{ac} \rightarrow Rh_2(PF_3)_6(\mu\text{-ac}) + 2PF_3 \quad (3)$$
(ac = HC_2H, $C_3H_5C_2H$, $C_6H_5C_2C_6H_5$, $CF_3C_2CF_3$, etc.)

However, there have been no published structural studies of $Rh_2(PF_3)_8$, and there are only two x-ray structural determinations on PF_3 complexes of the cobalt triad. The μ-diphenylacetylene complex $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$[4] is structurally similar to $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ and related bridging acetylene complexes derived from $Co_2(CO)_8$. The structure of $HCo(PF_3)_4$[5] can be described as a distorted trigonal bipyramid with the hydrogen atom occupying an axial position or as an essentially tetrahedral array of PF_3 groups with hydrogen in one of the tetrahedral faces.[6] The low-temperature limiting ^{19}F NMR spectra of $HM(PF_3)_4$ (M = Co, Rh, or Ir) show two sets of resonances in a 3:1 ratio,[6] indicating a structure with C_{3v} microsymmetry in solution. X-ray studies of many five-coordinate complexes of the type $YCo(CO)_4$, or ligand substitution products thereof, have shown the favored geometry to be trigonal bipyramidal with the anionic ligand Y in an axial position.[7] Dicobalt octacarbonyl itself has the CO-bridged structure I in the solid state[8], but in solution this is in equilibrium with an isomer containing no CO bridges, which is favored as the temperature is increased.[9,10] Although there has been disagreement about the structure of this isomer,[9,10] the most recent study[11] suggests structure IIa, consisting of two axially linked trigonal bipyramids (D_{3d} symmetry), as most likely, and this structure (IIb) is indeed adopted by $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$ in the solid state.[12] However, there is evidence for a small amount of a second "high-temperature" isomer of $Co_2(CO)_8$ which also contains no CO bridges.[11]



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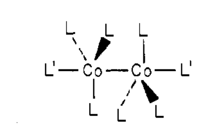


IIa, L = L′ = CO
b, L = CO; L′ = $P(n\text{-}C_4H_9)_3$
c, L = L′ = $P(OCH_3)_3$

Analogies with $HCo(PF_3)_4$, with related nonbridged carbonyl complexes, and with the recently synthesized trimethyl phosphite complexes $M_2[P(OCH_3)_3]_8$ (M = Co[13] or Rh[14]) (IIc) would certainly suggest structure II as the most likely for $Rh_2(PF_3)_8$.[15] Our investigation shows that this expectation is not borne out, either for $Rh_2(PF_3)_8$ or for its iridium analogue.

Experimental Section

The complexes $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ were prepared as described previously.[2] The monomeric complexes $HRh(PF_3)_4$ and $IrCl(PF_3)_4$

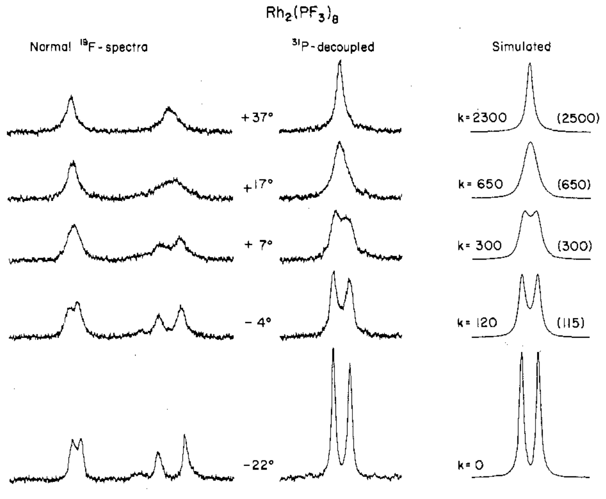


Figure 1. Normal and ^{31}P-noise-decoupled ^{19}F NMR spectra at 56.45 MHz of $Rh_2(PF_3)_8$ in C_6F_5Br at various temperatures with calculated NMR line shapes at rates (K) indicated.

were generated in situ in the NMR solvent by the reactions of hydrogen with $Rh_2(PF_3)_8$ and of PF_3 with $[IrCl(PF_3)_2]_2$, respectively.[2] Solvents were dried over molecular sieves, BDH 4A, except for CHF_2Cl which was condensed into the NMR tube directly from the cylinder.

Proton NMR spectra were measured on a Varian HA-100 instrument; fluorine and phosphorus NMR spectra were obtained at 56.45 and 24.29 MHz, respectively, on a modified JEOL C60-HL spectrometer. The methods of heteronuclear decoupling, temperature control and measurement, and line shape calculations have been described.[3]

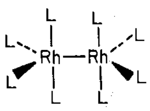
Results and Discussion

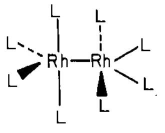
As reported previously[2] the ^{19}F NMR spectra of $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ at 24 °C consist of a broad doublet with a large splitting (~1400 Hz) typical of coordinated PF_3 groups. Each peak is asymmetric, but for $Rh_2(PF_3)_8$ the high-field peak is broader than the low-field peak, whereas for $Ir_2(PF_3)_8$ the two peaks exhibit a mirror-image pattern about the midpoint of the doublet. The spectrum of $Rh_2(PF_3)_8$, on warming to 50 °C, sharpens to give a pattern similar to that of $Ir_2(PF_3)_8$ at 24 °C. The change is reversible, showing that there is no decomposition in this temperature range. The spectrum of $Rh_2(PF_3)_8$, on cooling below 24 °C, broadens and at 10 °C peak separation is observed; the limiting spectrum is reached at about −15 °C (Figure 1). At this temperature the high-field half of the spectrum has three groups of resonances which integrate approximately as 2:9:11, and clearly the spectrum is too complex for any structural conclusions to be drawn. The behavior of $Ir_2(PF_3)_8$ is similar; the doublet broadens on cooling to 0 °C and a limiting spectrum is reached at about −15 °C, but the chemical shift difference between the various PF_3 groups is smaller than in $Rh_2(PF_3)_8$.

Table I. ^{19}F NMR Parameters[a]

Compd	Solvent	Temp, °C	ϕ_F (intens)	"J_{PF}"
$Rh_2(PF_3)_8$[b]	$CFCl_3$	24	2.8	1340
		−20	0.5 (1)	1220
			4.1 (1)	1370
$Ir_2(PF_3)_8$	C_6F_5Br	24	4.4	1240
		−20	4.0 (1)	1300
			4.6 (1)	1200
$HRh(PF_3)_4$	CHF_2Cl	−38	4.3	1275.1[c]
		−104	4.1 (3)	
			8.0 (1)[d]	
$IrCl(PF_3)_4$	$CFCl_3$	24	19.0	1265

[a] Chemical shifts (ϕ_F) in ppm upfield of internal $CFCl_3$, ±0.1 ppm; "J_{PF}" = $|^1J_{PF} + 3(^3J_{PF})|$ in Hz (±10 Hz). [b] δ_P (ppm downfield of external H_3PO_4) 114 ± 2; "J_{RhP}" = $|^1J_{RhP} + {}^2J_{RhP}|$ = 250 ±10 Hz. [c] Measured in CF_2Cl_2 on an HA-100 instrument at 94.1 MHz at 30 °C. Triplet due to couplings $J_{HF} = J_{RhF}$ = 16 Hz resolved at 30 and −4 °C. [d] J_{HF} or J_{RhF} = 28 Hz.


IIIa


IIIb

L = PF_3

The problem has been simplified by ^{31}P decoupling using noise-modulated irradiation at the ^{31}P resonance frequency.[3] In the slow-exchange limit both $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ clearly show two equally intense singlets (Figure 1 and Table I); no ^{103}Rh–^{19}F coupling could be resolved in the case of $Rh_2(PF_3)_8$. This result is not in accord with structure II, which would have been expected to show ^{19}F resonances in a 3:1 ratio arising from the equatorial and axial PF_3 groups, but it is accounted for if the two trigonal bipyramids are joined equatorially. The $(PF_3)_4$ units could then be either eclipsed (IIIa, D_{2h} microsymmetry) or staggered by 90° (IIIb, D_{2d} microsymmetry). The second alternative, which should be favored on steric grounds, has been confirmed by an x-ray examination of a poor-quality crystal of $Rh_2(PF_3)_8$.[16] The Rh–Rh distance [2.88 (2) Å] is longer than in $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(\mu\text{-}C_6H_5C_2C_6H_5)$ [2.740 (1) Å],[4] $Rh_4(CO)_{12}$ [average 2.73 Å],[17] and $Rh_6(CO)_{16}$ [2.776 (1) Å],[18] consistent with the ready cleavage of the metal–metal bond by hydrogen and group 4 hydrides.[2]

The ^{31}P NMR spectrum of $Rh_2(PF_3)_8$ at 24 °C consists of a very broad 1:3:3:1 quartet, each peak of which can just be resolved into a doublet. The ^{31}P{^{19}F} NMR spectrum simplifies to a well-resolved doublet [$|^1J_{RhP} + {}^2J_{RhP}|$ = 250 Hz[19]], showing that all of the ^{31}P nuclei are equivalent at 24 °C due to intramolecular exchange of PF_3 groups and also that intermolecular exchange of PF_3 groups must be slow on the NMR time scale. The fact that a doublet rather than a triplet is observed further indicates that there is no intramolecular exchange between the two rhodium atoms and that $|^1J_{RhP} - {}^2J_{RhP}| >> |^1J_{RhRh}|$.

The rates of PF_3 exchange for $Rh_2(PF_3)_8$ have been estimated from the ^{19}F{^{31}P} spectra at different temperatures by comparison with line shapes calculated for the AB ⇌ BA case with J_{AB} = 0; a suitable value of T_2 was used to account for the width of the NMR signals in the slow- and fast-exchange limits. A plot of log (rate) vs. $1/T$ was linear.[20] The rates were converted into free energies of activation using the Eyring equation

$$\text{rate } (K) = \kappa \frac{kT}{h} \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right)$$

in which the symbols have their usual meanings and the transmission coefficient, κ, is assumed to be 1. An independent estimate of the rate for $Rh_2(PF_3)_8$ at the coalescence temperature was made for the separate low-field and high-field halves of the normal ^{19}F spectrum using the equation

$$K = \pi(\nu_A - \nu_B)/2^{1/2}$$

The value of $\Delta G^{\ddagger}$ derived in this way agrees well (within 0.2 kcal/mol) with that obtained from line shape analysis (Table II). In the case of $Ir_2(PF_3)_8$, the chemical shift difference in the ^{19}F{^{31}P} limiting spectrum was only 0.6 ppm, and line shape analysis was not feasible. However, the different values of "J_{PF}" for the dissimilar PF_3 groups give rise to separations larger than this in the low-field and high-field halves of the ^{19}F spectrum, and hence for $Ir_2(PF_3)_8$ the estimated $\Delta G^{\ddagger}$

Table II. Parameters for Intramolecular Exchange of Trifluorophosphine Ligands

Compd	Solvent	Temp range, °C[a]	Range of rates, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
$Rh_2(PF_3)_8$	C_6F_5Br	−7 to +37	75–2300	13.21 ± 0.05[b]
$Ir_2(PF_3)_8$	C_6F_5Br	Coalescence, 0	225[c]	13.0 ± 0.5
$HRh(PF_3)_4$	CHF_2Cl	−78.5 to −56.5	40–1200	9.66 ± 0.02[d]

[a] Range over which rates could be estimated. [b] At 7 °C from best fit of Arrhenius plot; $\Delta H^{\ddagger} = 12.6 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -2.2 \pm 2.5$ cal/(deg mol). Values for $\Delta G^{\ddagger}$ of 13.0 and 13.1 kcal/mol, respectively, were obtained from the rates estimated at the coalescence temperatures of the low-field and high-field halves of the normal ^{19}F spectrum (see text). [c] Rate estimated at the coalescence temperature of the low-field half of the normal ^{19}F spectrum. [d] At −68 °C from best fit of Arrhenius plot; $\Delta H^{\ddagger} =$ 13.0 ± 0.5 kcal/mol, $\Delta S^{\ddagger} = 16.5 \pm 2.5$ cal/(deg mol).

(Table II) is based only on the measurement of the coalescence temperature in the normal ^{19}F spectrum. The justification for treating the halves of the ^{19}F spectrum separately has been discussed elsewhere.[3]

As a check on structural conclusions based on $^{19}F\{^{31}P\}$ NMR spectra, we have reexamined $HRh(PF_3)_4$, the variable-temperature ^{19}F NMR spectrum of which has been reported by Meakin et al.[6] The 56.45-MHz ^{19}F spectrum at the slow-exchange limit is very complex, and the separate axial and equatorial ^{19}F resonances cannot be readily distinguished. The larger chemical shifts obtained at 84.66 MHz enabled Meakin et al.[6] to show that the ratio of PF_3 groups is 3:1, consistent with a structure of C_{3v} microsymmetry, and to estimate the rates of intramolecular exchange at different temperatures. The $^{19}F\{^{31}P\}$ spectrum of $HRh(PF_3)_4$ in the slow-exchange limit (Figure 2) shows the expected two resonances in a 3:1 ratio due to the equatorial and axial PF_3 groups, the former being a singlet and the latter a doublet (J_{HF} or J_{RhF} = 28 Hz). On warming of $HRh(PF_3)_4$ to room temperature, these signals coalesce and finally sharpen to a singlet; the expected triplet due to the fortuitously equal couplings J_{HF} and J_{RhF} of 16 Hz is not resolved. Accurate rates of exchange obtained by line shape analysis of the $^{19}F\{^{31}P\}$ NMR spectrum using the assumptions already discussed gave an excellent linear log (rate) vs. $1/T$ plot. Activation parameters are in Table II. The free energy of activation, $\Delta G^{\ddagger}$, of 9.66 ± 0.02 kcal/mol at −68 °C is in fair agreement with the value of 9.0 kcal/mol at an unspecified temperature given previously,[6] though our result is probably more accurate. The results for $HRh(PF_3)_4$ add credibility to the conclusions derived from the $^{19}F\{^{31}P\}$ spectra of $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$.

We have also studied the variable-temperature ^{19}F NMR spectrum of $IrCl(PF_3)_4$[2] in an effort to gain structural information. In $CFCl_3$ at 27 °C the spectrum is broadened by intermolecular exchange with free PF_3, and, although resolution is improved on cooling, a low-intensity doublet due to free PF_3 appears only at −60 °C. The spectrum consists of a pair of mirror-imaged multiplets separated by 1265 Hz due to $|^1J_{PF} + 3^3J_{PF}|$ and centered at 19.0 ppm upfield of $CFCl_3$; this remains unchanged down to −66 °C in $CFCl_3$ and −85 °C in CHF_2Cl. Thus the PF_3 groups show time-averaged equivalence owing to intramolecular exchange[21] and, in agreement, the $^{19}F\{^{31}P\}$ spectrum in $CFCl_3$ at −30 °C is a sharp singlet. At −100 °C in CHF_2Cl containing a trace of $CFCl_3$ some broadening of the ^{19}F spectrum is evident, perhaps owing to slowing of intramolecular exchange (the solvent signals remain sharp at this temperature), but the tendency of $IrCl(PF_3)_4$ to crystallize from solution has prevented further study.

Although no unique mechanism for the averaging of PF_3 environments in $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ can be given, an attractive possibility is the Berry mechanism, in which the metal–metal bond acts as a pivot and the metal–phosphorus bonds bend until the PF_3 groups are in the equivalent basal positions of a square pyramid about each metal atom; this transition state could have D_{4h} or D_{4d} microsymmetry. The close similarity of the $\Delta G^{\ddagger}$ values for $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ is surprising in view of the general trend toward higher barriers to intramolecular rearrangement processes with increasing atomic weight in a given triad, e.g., for the $HM(PF_3)_4$ complexes (M = Co, Rh, or Ir).[6]

Figure 2. Normal and ^{31}P-noise-decoupled ^{19}F NMR spectra at 56.45 MHz of $HRh(PF_3)_4$ in CHF_2Cl at various temperatures with calculated NMR line shapes at rates (*K*) indicated.

We can see no obvious simple reason that $Rh_2(PF_3)_8$ and $Ir_2(PF_3)_8$ should adopt the equatorially linked bi(trigonal-bipyramidal) structure IIIb in preference to the axially linked structure II.[22] It could be argued that steric repulsion between the bulky PF_3 groups across the metal–metal bond is less in IIIb than in II. This reasoning ignores the interligand repulsions on each metal atom, which may well be equally or more significant; moreover, it fails to explain why $Co_2[P(OCH_3)_3]_8$ and $Rh_2[P(OCH_3)_3]_8$ adopt structure II even though trimethyl phosphite (cone angle 107 ± 2°)[23] is bulkier than trifluorophosphine (cone angle 104 ± 2°).[23] The fact that these trimethyl phosphite complexes are stereochemically rigid up to ~100 °C[13,14] is also in marked contrast with the behavior of the trifluorophosphine complexes and is probably a consequence of the different ground-state geometries. Since the metal–metal bond in $M_2[P(OCH_3)_3]_8$ occupies the axial position of a trigonal bipyramid, it cannot act as the pivot for the usual Berry mechanism. This mechanism would involve bending the bulky $M[P(OCH_3)_3]_4$ unit using an equatorial trimethyl phosphite as pivot, clearly an unfavorable process.

Acknowledgment. We thank Dr. W. S. Sheldrick, Gesellschaft für Molekularbiologische Forschung mbH, Stockheim über Braunschweig, Germany, for his crystallographic examination of $Rh_2(PF_3)_8$ and for helpful correspondence.

Registry No. $Rh_2(PF_3)_8$, 14876-96-1; $Ir_2(PF_3)_8$, 34228-57-4; $HRh(PF_3)_4$, 16949-48-7; $IrCl(PF_3)_4$, 34344-34-8; ^{31}P, 7723-14-0.

Supplementary Material Available: Arrhenius plots for $Rh_2(PF_3)_8$ and $HRh(PF_3)_4$ (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Th. Kruck, N. Derner, and W. Lang, *Z. Naturforsch., B*, **21**, 1020 (1966).
(2) M. A. Bennett and D. J. Patmore, *Inorg. Chem.*, **10**, 2387 (1971).
(3) M. A. Bennett, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, **15**, 90 (1976).
(4) M. A. Bennett, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Inorg. Chem.*, **15**, 97 (1976).
(5) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **9**, 2403 (1970).
(6) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 1797 (1971); P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, **94**, 5271 (1972).
(7) J. S. Wood, *Prog. Inorg. Chem.*, **16**, 227 (1972), and references cited therein.
(8) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).
(9) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); *Helv. Chim. Acta*, **47**, 1064, 1555 (1964).
(10) G. Bor, *Spectrochim Acta*, **19**, 2065 (1963).
(11) G. Bor and K. Noack, *J. Organomet. Chem.*, **64**, 367 (1974).
(12) J. A. Ibers, *J. Organomet. Chem.*, **14**, 423 (1968).
(13) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **95**, 5419 (1973); **96**, 7920 (1974).
(14) R. Mathieu and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 147 (1974).
(15) A structure containing PF_3 bridges is most unlikely, since PF_3 ligand exchange between metal atoms is not observed in the μ-acetylene complexes $Rh_2(PF_3)_6(ac)^3$ or in $Rh_2(PF_3)_8$ (this work).
(16) W. S. Sheldrick, personal communication. In addition to problems caused by poor crystal quality, there was evidence in the difference Fourier synthesis of thermal motions and of considerable disorder in the fluorine atoms. A low-temperature study of $Rh_2(PF_3)_8$ is planned.
(17) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).
(18) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).
(19) The Rh_2P_8 unit constitutes an $AA'X_nX'_n$ spin system ($n = 4$), for which the separation of the main doublet is $|J_{AX} + J_{AX'}|$: R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(20) The Arrhenius plots for $Rh_2(PF_3)_8$ and $HRh(PF_3)_4$ have been included as supplementary material.
(21) A referee has noted that a square-pyramidal geometry for $IrCl(PF_3)_4$, with axial Cl, would also be consistent with the observation of equivalent PF_3 groups. This seems to us unlikely because trigonal-bipyramidal geometry has so far been observed for all compounds studied of the type $YCo(CO)_4$ (Y = various anionic ligands).[7]
(22) It is tempting to suggest that the second "high-temperature" isomer of $Co_2(CO)_8$[11] has the equatorially linked bi(trigonal-bipyramidal) structure.
(23) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

Contribution from the Department of Chemistry,
Grinnell College, Grinnell, Iowa 50112

Stereochemistry of the Reaction of Dimethyl Sulfoxide with Dichloro(glycinato)platinate(II) and Similar Amino Acid Complexes

Luther E. Erickson* and William F. Hahne

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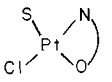
In a recently reported NMR study of the kinetics and stereochemistry of the reaction of K[Pt(amino acid)Cl_2] with dimethyl sulfoxide (DMSO) to form Pt(amino acid)-(DMSO)Cl, we concluded that the thermodynamically preferred isomer of Pt(N–O)(DMSO)Cl is I when N–O = gly



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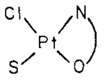
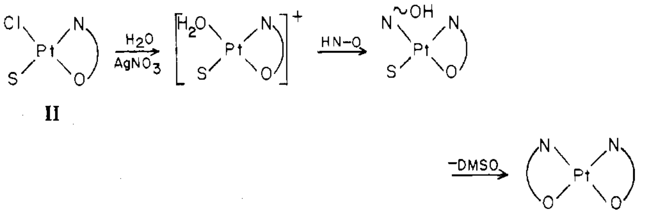


II

or aba.[1,2] We concluded further that the single isomer of Pt(ala)(DMSO)Cl obtained by Kukushkin and Gur'yanova[3] by five different reactions was erroneously identified as II, in which DMSO is trans to N. This note reports results of additional NMR experiments which confirm these conclusions and establish the source of discrepancy between the two assignments.

Scheme I. Reaction Sequence Used in Assignment of Structure II by Kukushkin and Gur'yanova[3]



Kukushkin and Gur'yanova based their assignment of structure II to Pt(ala)(DMSO)Cl on the following chemical argument, which is summarized in Scheme I. The chloro complex was first converted by treatment with aqueous $AgNO_3$ to the corresponding aquo complex, which was subsequently converted to $Pt(ala)_2$ by addition of a second mole of alanine. Reaction of the $Pt(ala)_2$ with thiourea was used to demonstrate that it was the cis isomer,[4] from which they concluded that the original chloro complex had structure II. This assignment assumed (a) that water replaces Cl^- of the complex with retention of configuration and (b) that the nitrogen of the second alanine molecule added displaces the water molecule of the aquo complex before the ring closure which eliminates DMSO. Evidence will be introduced to show that assumption (b) is not correct.

Experimental Section

Preparation of K[Pt(DMSO)Cl_3]. A 0.25 M stock solution of K[Pt(DMSO)Cl_3] in D_2O was prepared by adding 6.25 mol of DMSO to 6.25 mmol of K_2PtCl_4 in 20 ml of D_2O and diluting to 25.0 ml.[5] The proton NMR spectrum was monitored as free DMSO was converted essentially completely to $[Pt(DMSO)Cl_3]^-$ (δ 0.80 ppm downfield from free DMSO; $^3J_{Pt-S-CH_3} = 24$ Hz).

Reactions of K[Pt(DMSO)Cl_3] with Glycinate and Other Amino Acid Anions. One millimole of NaOH was added to 1 mmol of free amino acid. The solution was then evaporated to dryness, treated once with 1 ml of D_2O, and evaporated to dryness again to ensure complete exchange of amino protons. Four milliliters of 0.25 M K[Pt(DMSO)Cl_3] was added to dissolve the solid salt and the NMR spectrum of the solution was monitored as the reaction proceeded.

Preparation of $[Pt(aba)(DMSO)(OD_2)]^+$. One millimole of $AgNO_3$ in 5 ml of D_2O was added to 1 mmol of Pt(aba)(DMSO)Cl and the suspension was stirred with warming for about 4 h to precipitate AgCl which was removed by filtration through sintered glass. The NMR spectrum was recorded and the solution was than evaporated to dryness to yield 1 mmol of solid $[Pt(aba)(DMSO)(OD_2)]NO_3$.

Reaction of $[Pt(aba)(DMSO)(OD_2)]^+$ with Methylamine. The above described solid $[Pt(aba)(DMSO)(OD_2)]NO_3$ was dissolved quickly in 4 ml of a solution containing 0.25 M NaOD and 0.25 M methylamine in D_2O. The latter solution was prepared by treating 10 mmol of methylamine hydrochloride with 10 mmol of silver nitrate in D_2O to remove the chloride as AgCl and then adding 20 mmol (5 ml of 4 M) NaOD before diluting to 40 ml. The OD^- was included to neutralize the acidic proton of coordinated D_2O ($pK_a \simeq 4.4$).[3]

Results and Conclusions

Reaction of K[Pt(DMSO)Cl_3] with Amino Acid Anions. Spectral changes associated with the reaction of K[Pt-(DMSO)Cl_3] with glycinate anion are illustrated in Figure 1. The spectrum of the freshly mixed solution shows the two strong 1:4:1 triplets (central peak and platinum-195 satellites) typical of coordinated glycinate ($^3J_{Pt-N-C-H} = 28$ Hz) and coordinated DMSO ($^3J_{Pt-S-CH_3} = 20.4$ Hz) and a much smaller peak at δ 0.85 ppm (from free DMSO). After warming of the solution for 5 min at 80 °C, the original triplets have decreased to about half their original intensity while the peak at δ 0.85 has increased correspondingly and a new peak