Studies on the reactivity of these Pt and Pd dicarbonyl complexes with neutral and anionic ligands are in progress.

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Application of 2-D NOE Phosphorus-31 NMR Spectroscopy in Determining Rearrangement Mechanisms of Stereochemically Nonrigid, Octahedral Organometallic Complexes

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Summary: 2-D NOE phosphorus-31 NMR spectroscopy has been used to illustrate definitively, for the first time, that stereochemically nonrigid, octahedral organometallic complexes such as $Cr(CO)_{5-n}(CX)[(RO)_3P]_n$ (R = alkyl, aryl; X = O, n = 2, 3; X = S, Se, n = 1–3) undergo rearrangement intramolecularly with trigonal-prismatic pathways being exclusively followed for the tris(tertiary phosphite) thio- and selenocarbonyl derivatives. This new spectroscopic approach should prove applicable to many other stereochemically nonrigid organometallic systems containing suitable NMR spin labels.

Ever since the discovery that many organometallic complexes are stereochemically nonrigid in solution, chemists have sought to establish the mechanisms by which these processes occur.[1] Group 6[13] metal octahedral complexes such as $Cr(CO)_4[C(OMe)Me](PR_3)$ (R = Et, C_6H_{11}),[2] $W(CO)_4(^{13}CO)(CS)$,[3] and $M(CO)_{6-n}(PR_3)_n$ (M = Cr, Mo, W; R = Me, Et, n-Bu, OMe, OEt; n = 1–2)[4] are postulated to rearrange intramolecularly through either trigonal-prismatic or bicapped-tetrahedral intermediates. We now report a surprisingly simple use of 2-D NOE ^{31}P NMR spectroscopy in studying the rearrangement dynamics of organometallics and show how it is possible to choose unambiguously between the different mechanistic routes possible. 2-D ^1H and ^{13}C NMR techniques have recently been employed to examine the chemical exchange networks of organometallic complexes,[5] but our work appears to be the first for ^{31}P nuclei.

The chalcocarbonyl complexes examined in this investigation were of the general formula $Cr(CO)_{5-n}(CX)[(RO)_3P]_n$ (R = alkyl or aryl; X = O, S, Se; n = 1–3). However, for the purposes of this communication, we will describe our 2-D NMR approach only for the $Cr(CO)_2(CX)[(RO)_3P]_3$ (X = O, S, Se) derivatives[6,7] but similar results have been obtained for the other systems.

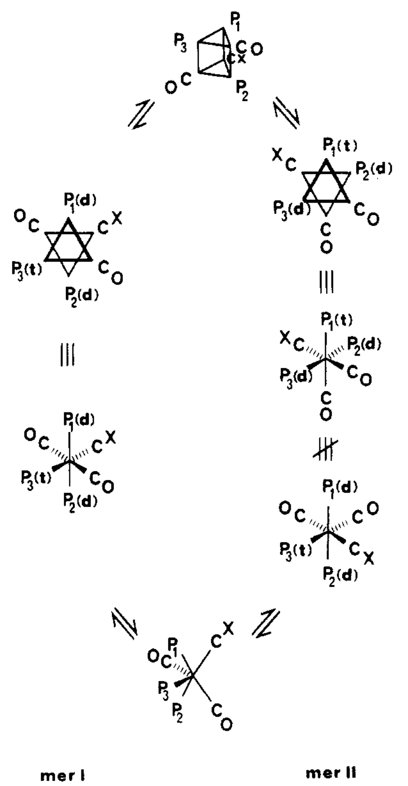
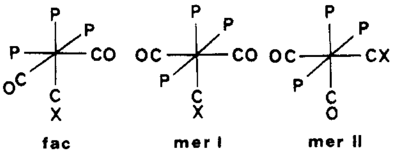


Figure 1. Possible mechanisms for the interconversion of the *mer*-I and *mer*-II $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) isomers. The MeO groups have been omitted for the sake of clarity.



2-D ^{31}P NMR experiments demonstrated that dynamic intramolecular interconversions are taking place between the *mer*-I and *mer*-II isomers[8,9] of the thio- and selenocarbonyl complexes on the time scale of the measurements at temperatures above 50 °C. However, no *fac* to *mer*-I or *fac* to *mer*-II isomerization was observed at temperatures up to 80 °C, while higher temperatures resulted in sample decomposition.

The 2-D NMR studies of the *mer*-I to *mer*-II isomerizations for the $Cr(CO)_2(CX)[(CH_3O)_3P]_3$ (X = S, Se) complexes provide for the first time a definite choice between the bicapped-tetrahedral and trigonal-prismatic pathways (Figure 1). The bicapped tetrahedron mecha-

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[1] (a) Muetterties, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5097. (b) Meakin, P.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 75. (c) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1975**, *98*, 2484.

[2] (a) Fischer, H. F.; Fischer, E. O.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 644; *J. Organomet. Chem.* **1974**, *73*, 331.

[3] Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1975**, *98*, 4110.

[4] See, for example: Darensbourg, D. J.; Gray, R. L. *Inorg. Chem.* **1984**, *23*, 2993 and references to earlier work by this group.

[5] (a) Benn, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 626. (b) Kook, A. M.; Nicklas, P. N.; Selegue, J. P.; Smith, S. L. *Organometallics* **1984**, *3*, 499.

[6] *fac*-$Cr(CO)_3[(RO)_3P]_3$ was prepared by using the procedure of Pidcock, A.; Taylor, B. W. *J. Chem. Soc. A* **1967**, 877. The *mer* isomer was obtained by subsequent heating of the *fac* isomer at 70 °C to yield a *fac*-to-*mer* ratio of 5:1 at equilibrium in approximately 3 h.

[7] The CS and CSe complexes were prepared by arene displacement from (η-arene)$Cr(CO)_2(CX)$ (X = S, Se). (a) Bird, P. H.; Ismail, A. A.; Butler, I. S. *Inorg. Chem.* **1985**, *24*, 2911. (b) Ismail, A. A.; Butler, I. S.; Bonnet, J.-J.; Askenazy, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* in press.

[8] The intramolecular nature of the process was demonstrated by the lack of correlation in 2-D NMR between resonances of the complexes and those of excess $(MeO)_3P$ present in solution. In addition, monitoring the isomerization of the complexes by FT-IR spectroscopy in the presence of excess $(PhO)_3P$ established that no incorporation of $(PhO)_3P$ occurred.

[9] For $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) K_{eq}(*mer*-I/*fac*) = 5.0 and K_{eq}(*mer*-I/*mer*-II) = 20.3. These values were calculated from the ^{31}P NMR spectra in the absence of NOE (delay time > $10T_1$). The equilibrium constants for the species are temperature independent between 20 and 80 °C.

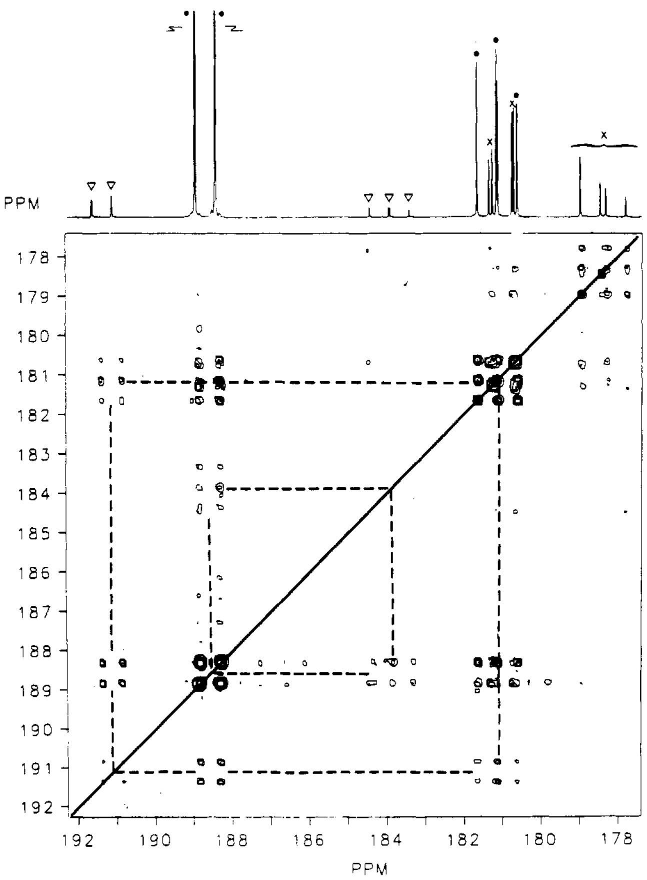

Figure 2. 2-D ^{31}P contour map for $Cr(CO)_2(CS)[MeO)_3P]_3$ in deuteriotoluene at 61 °C on a Varian XL-300 spectrometer. An NOE accordion pulse sequence ($\pi/2$, t_1, $\pi/2$, mix, π, t_2; see ref 12) was employed with a repetition delay of 2 s and incrementing the mixing time according to the equation $t_{mix} = \kappa t_1$ with $\kappa = 30$. All three isomers exhibit an AB_2 coupling pattern (chemical shifts are relative to H_3PO_4 as external standard): ▽, *mer*-II P_2, P_3 (d) 191.4 ppm, P_1 (t) 184.0 ppm (J = 64 Hz); ●, *mer*-I P_2, P_3 (d) 188.6 ppm, P_1 (t) 181.2 ppm (J = 64 Hz); X, *fac* P_2, P_3 (d) 181.1 ppm, P_1 (t) 178.5 ppm (J = 72 Hz). The assignments given for the resonances are based on those for the parent tricarbonyl complexes: Mathieu, R.; Lenzi, M.; Poilblanc, R. *Inorg. Chem.* **1970**, *9*, 2030 and the chemical shielding effects anticipated for the replacement of CO by CS or CSe.[7a]

nism would preserve the coupling pattern for each phosphorus nucleus in the two isomers while, for the trigonal-prismatic twist, the triplet would become a doublet and the doublet of the trans phosphorus atom would be transformed into a triplet. The resulting 2-D NMR spectra illustrate both NOE and chemical exchange between the phosphorus nuclei of the same molecule by the distinct symmetrical off-diagonal contour on the exchange map[10] (Figure 2). More importantly, however, the exchange of the *mer*-I to *mer*-II isomer provides convincing proof of dynamic rearrangement via a trigonal prism rather than a bicapped tetrahedron, as seen from the correlation of the off-diagonal peak of the doublet of the *mer*-II (bottom left-hand side of the contour map) to the doublet and triplet of *mer*-I, while the triplet of the *mer*-II is exchanging with the doublet of *mer*-I. The *mer*-I to *fac* or *fac* to *mer*-II rearrangement can be envisaged to take place by a further twist involving another trigonal-prismatic intermediate. This possibility is supported by the lack of distortion in the X-ray structures of the two *mer*-I complexes[7] and the activation parameters obtained for the *mer*-I to *fac* isomerization of the CSe complex.[11]

In conclusion, 2-D NMR spectroscopy is proving to be extremely useful in mechanistic studies of sterochemically nonrigid organometallic systems, especially since useful information on the rearrangements may be obtained even in situations when the more usual technique of NMR line-shape analysis is not possible because of no signal coalescence being observed. Further work is in progress on the utility of ^{31}P and ^{13}C 2-D NOE NMR spectroscopy in this area.

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[10] The observation of an off-diagonal correlation between the doublet and triplet of the *fac* isomer in Figure 2 may be due to chemical exchange between equivalent *fac* isomers. However, the possibility that the observed correlation is solely due to NOE cannot be ruled out in this case.

[11] The kinetics of the intramolecular isomerization (*mer*-I to *fac* isomer) has been monitored by variable-temperature FT-IR spectroscopy: $\Delta H^* = 15.5 \pm 0.3$ kcal mol^{-1}; $\Delta S^* = -28.0 \pm 1$ eu.

[12] Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1304.

[13] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13).