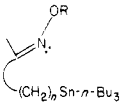
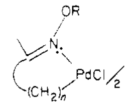
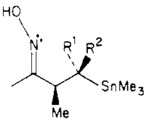
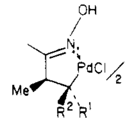
Table I. Cyclopalldation with the Stannyl Ketoximes[a]

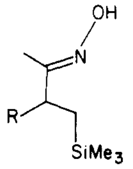
run	substrate (n, R)	product[b] (ratio)[c]	yield,[d] %	mp, °C (dec)	color
					
1	**1** (2, H)	**5**	76	136-139	pale yellow
2	**2** (2, Ac)	**6**	71	143-144	pale orange
3	**3** (3, H)	**7**	74	105-107	pale yellow
4	**4** (3, Ac)	**8**	75	122-125	pale orange
	 **9**, R¹=Me, R²=H **10**, R¹=H, R²=Me **11**, R¹=Ph, R²=H **12**, R¹=H, R²=Ph	 **13**, R¹=Me, R²=H **14**, R¹=H, R²=Me **15**, R¹=Ph, R²=H **16**, R¹=H, R²=Ph			
5	**9**	**13**:**14** (56:44)	90[e]		
6	**10**	**13**:**14** (60:40)	91[e]		
7	**11**	**15**:**16** (89:11)	95		
8	**12**	**15**:**16** (100:0)	87		

[a] The substrate (0.5-1.0 mmol), CH_2Cl_2 (2-4 mL), 0 °C, 30 min. [b] After concentration of the mixture under reduced pressure, addition of ether gave the crude product. Filtration, redissolution in CH_2Cl_2 (2 mL), and addition of ether gave the almost pure product. The products are stable in solid state or neat. Microanal. Found for **5** (Calcd): C, 21.08 (21.07); H, 3.55 (3.54); N, 6.04 (6.14). Found for **6** (Calcd): C, 26.61 (26.69); H, 3.60 (3.73); N, 4.91 (5.19). Found for **7** (Calcd): C, 24.73 (24.82); H, 4.04 (4.17); N, 5.75 (5.79). Found for **8** (Calcd): C, 29.60 (29.60); H, 4.18 (4.26); N, 4.83 (4.93). [c] Determined by ¹H NMR. [d] Isolated yields. [e] $PdCl_2(CH_3CN)_2$ was used; room temperature, 30 min.

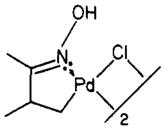
to our observations, Stille's procedure for the palladium-catalyzed coupling reaction with homotetraalkyltins in a polar solvent requires a much higher temperature.[6] Cyclopalladation of a sterically hindered alkyl oximes has been reported to require 2 days or more at room temperature.[2d]

Other examples include the α,β-disubstituted oximes **9**-**12**[7] which afforded the transmetalized complexes **13**-**16** (runs 5-8). The dimethyl oximes **9** and **10** gave the mixture of the cis and trans complexes **13** and **14**.[8] While both isomers **11** and **12** gave the trans disubstituted oxime complex **15**[9] predominantly. These stereochemical outcomes were interpreted as follows: (1) an equilibrium isomerization involving β-hydrogen elimination of the initially forming product followed by hydrogen insertion; (2) the transmetalation could proceed by both retention and inversion process of the C-Sn bond (Chart I).[10]

In place of the tributylstannyl function, a trimethylsilyl group can act as a directing group. Treatment of the (E)-β-silyl ketoxime **17** with dichlorobis(benzonitrile)palladium in dichloromethane *at room temperature for 1 day* gave **5** in 50% yield but contaminated with butanoxime complex derived from protonation of **5**.[11] Introduction of one α-methyl group on the silyl ketoxime as shown in **18** increases the yield of the corresponding cyclometalated product **19**[12] in 88% yield as a pure form,[13] since the **19** is more stable than **5** for prolonged reaction time.



17, R=H
18, R=Me



19

Thus we have demonstrated a new cyclopalladation reaction with organostannyl or organosilyl groups as a directing group in chelation systems of oximes.

---

(6) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (b) Tanaka, M. *Tetrahedron Lett.* **1979**, 2601. (c) Kosugi, M.; Shimizu, Y.; Migita, T. *J. Organomet. Chem.* **1977**, *129*, C36.

(7) For the starting ketones, see: Fleming, I.; Urch, C. J. *Tetrahedron Lett.* **1983**, *24*, 4591.

(8) ¹H NMR (90 MHz, $CDCl_3$): δ 0.71 (d, J = 7.2 Hz, **14**, H_3CCPd), 0.90 (d, J = 7.0 Hz, **13**, H_3CCPd), 1.21 (d, J = 7.2 Hz, 3 H, **13** and **14** $H_3CCC{=}N$), 1.91 (s, **13**, $H_3CC{=}N$), 1.92 (s, **14**, $H_3CC{=}N$), 1.97 (m,1 H, HCPd), 3.02 (double q, J = 7.0 × 3 and 3.8 Hz, **13**, HCC=N), 3.57 (double q, J = 7.2 × 3 and 5.7 Hz, **14**, HCC=N), 8.23 (br, 1 H, HON).

(9) ¹H NMR (90 MHz, $CDCl_3$): δ 0.98 (d, J = 7.4 Hz, **16**, H_3CCPd), 1.32 (d, J = 7.0 Hz, **15**, H_3CCPd), 2.00 (s, **15** and **16**, 3 H, $H_3CC{=}N$), 2.25 (m, **15** and **16**, 1 H, HCCC=N), 4.08 (d, J = 2.5 Hz, **15**, HCCPd), 4.34 (d, J = 7.0 Hz, **16**, HCCPd), 7.18 (m, 5 H, Ph), 8.05 (br, 1 H, HON).

(10) Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177. Olszoy, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1676. Also see ref 7.

(11) The decomposition could be attributable to formation of hydrogen chloride by reactions of hydroxy moiety of the oxime and generated trimethylchlorosilane for long reaction periods.

(12) ¹H NMR (60 MHz, $CDCl_3$): δ 1.24 (d, J = 7.2 Hz, 3 H, $H_3CCC{=}N$), 1.93 (s, 3 H, $H_3CC{=}N$), 2.20 (m, 2 H), 2.92 (m, 1 H), 7.95 (br, 1 H, HON). Microanal. Found (Calcd): C, 24.79 (24.82); H, 4.19 (4.17); N, 5.66 (5.59).

(13) In place of the stannyl ketoximes **9**-**11**, the corresponding silyl derivatives was treated with dichlorobis(benzonitrile)palladium but gave only dichlorooxime complexes. Expected transmetalation was not observed.

Neutral Bis(perhalophenyl)dicarbonylpalladium(II) and -platinum(II) Complexes

Rafael Usón,* Juan Forniés, Milagros Tomás, and Babil Menjón

Departamento de Química Inorgânica
Universidad de Zaragoza
50009 Zaragoza, Spain

Received April 29, 1985

Summary: Normal pressure carbonylation of *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ (M = Pd, Pt; X = F, Cl; OC_4H_8 = tetrahydrofuran) leads to the isolation of *cis*-$[M(C_6X_5)_2(CO)_2]$. High ν(CO) stretching bands (far-IR, 2186 cm^{-1} for M = Pd and X = F) point to negligible metal-to-CO π-back-bonding.

0276-7333/85/2304-1912$01.50/0

Table I. Some IR Relevant Data and Melting Points

		$\nu(C{\equiv}O)$				
	cis-$M(C_6X_5)_2L_2$	sym	asym	X-sensitive (C_6X_5)[9]	$\nu(MC_R)$[10] (R = C_6Cl_5)	mp, °C
I	$Pd(C_6F_5)_2(OC_4H_8)_2$			802, 792		100 dec
II	$Pd(C_6Cl_5)_2(OC_4H_8)_2$			841, 832	627, 617	94 dec
III	$Pt(C_6F_5)_2(OC_4H_8)_2$			818, 806		139 dec
IV	$Pt(C_6Cl_5)_2(OC_4H_8)_2$			[a]	637,[b] 631	144 dec
V	$Pd(C_6F_5)_2(CO)_2$	2186	2163	798, 786		
VI	$Pd(C_6Cl_5)_2(CO)_2$	2173	2152	840, 833	619, 614	
VII	$Pt(C_6F_5)_2(CO)_2$	2174	2143	804, 792[b]		205[c]
VIII	$Pt(C_6Cl_5)_2(CO)_2$	2160	2126	847, 842	629, 623	208 dec

[a] The presence of a very strong absorption due to the OC_4H_8 precludes the assignment. [b] Shoulder. [c] Sublimes.

No monomeric dicarbonylpalladium(II) derivatives have been reported so far,[1] and only four dicarbonyl platinum(II) complexes have been described. *cis*-$[PtX_2(CO)_2]$ complexes (X = Cl,[2,3] Br,[2] I[2]) were prepared at high pressure (40–120 atm) and at temperatures over 100 °C, and recently reported[4] *trans*-$[PtCl_2(CO)_2]$, which readily isomerizes to the cis derivative, was synthesized at atmospheric pressure and low temperature (−80 °C).

We now report four new compounds, *cis*-$[M(C_6X_5)_2(CO)_2]$ (M = Pd, Pt; X = F, Cl), which have been synthesized under very mild conditions by carbonylation of the corresponding *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ complexes (OC_4H_8 = tetrahydrofuran) in dichloromethane solution. Other syntheses employing these starting materials are presently under study in our laboratory.

The starting complexes can be obtained by reacting the anionic $[NBu_4]_2[M(\mu\text{-}Cl)(C_6X_5)_2]_2$ compounds[5,6] with $AgClO_4$.

$$2AgClO_4 + [NBu_4]_2[M(\mu\text{-}Cl)(C_6X_5)_2]_2 \xrightarrow{THF} 2AgCl + 2(NBu_4)ClO_4 + 2\ cis\text{-}[M(C_6X_5)_2(OC_4H_8)_2] \quad (1)$$

Evaporation of the solution to dryness and addition of diethyl ether leave a residue of the insoluble AgCl plus $(NBu_4)ClO_4$. Upon evaporation of the filtered ether solution the stable, neutral *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ (M = Pd, X = F (I); M = Pd, X = Cl (II); M = Pt, X = F (III); M = Pt, X = Cl (IV)) derivatives can be isolated.[7]

Bubbling carbon monoxide through dichloromethane solutions of the *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ (I–IV) precursors results in precipitation of the *cis*-$[M(C_6X_5)_2(CO)_2]$ dicarbonyl derivatives (eq 2).

$$cis\text{-}[M(C_6X_5)_2(OC_4H_8)_2] \xrightarrow{CO} [M(C_6X_5)_2(CO)_2] \quad (2)$$

M = Pd; X = F (V) (66% yield), Cl (VI) (50% yield)

M = Pt; X = F (VII) (79% yield), Cl (VIII) (91%yield)

A rather general feature in palladium and platinum chemistry is the higher stability of the platinum compounds of a given type. Thus, reaction 2 takes place at room temperature and atmospheric pressure for the platinum compounds, but a lower temperature (−78 °C for X = F; −50 °C for X = Cl) is necessary for the syntheses of the palladium derivatives, which are subsequently filtered and washed with *n*-hexane (at the same temperature) and finally vacuum dried.

In fact, the platinum complexes are much more stable than the palladium ones. Complexes VII and VIII are stable even in moist air, as are their solutions in noncoordinating solvents. In OC_4H_8 solution one CO group is displaced by a solvent molecule, more slowly in the C_6Cl_5 than in the C_6F_5 derivative. The palladium(II) complexes V and VI are, however, only moderately stable at −30 °C under CO (they become gray after 10 h (V) or, respectively, several days (VI)), less stable under N_2 atmosphere, and unstable, even at −30 °C, in the presence of moisture. However, satisfactory analytical results have been obtained for the four (V–VIII) complexes.[7]

Table I collects some relevant IR data. All the complexes (I–VIII) show two absorptions corresponding to the X-sensitive modes of the C_6F_5 or C_6Cl_5 groups.[8,9] The pentachlorophenyl derivatives (II, IV, VI, VIII) also show two bands in the ν(MC) region.[10] Two very strong absorptions due to the ν(CO) modes can be observed in complexes V–VIII. All these features show these complexes to be the cis isomers (point group C_{2v}, ν(MC) modes, ν(CO) modes, $A_1 + B_1$ both IR actives).

The high frequencies of the first ν(CO) band are noteworthy. They are higher indeed than for free CO (2143 cm^{-1}). In particular, the ν(CO) values for the Pd derivatives are the highest so far reported for palladium or platinum(II) derivatives.[1,4,11,12]

This observation seems to indicate a very low degree of metal-to-carbon π-back-bonding that must be negligible in the palladium complexes. The low stability of the Pd complexes is not due to an intrinsically thermodynamic instability[13] but to the lability of the Pd(II)–CO bond.

The *cis*-$[Pd(C_6X_5)_2(CO)_2]$ complexes are the only mononuclear Pd dicarbonyls so far reported. During the preparation[11] of the binuclear $[Pd(\mu\text{-}Cl)Cl(CO)]_2$ (by carbonylation of $PdCl_2$ in $SOCl_2$ at 120 °C and 50 atm) the authors were not able to obtain any IR evidence for the presence of a $[PdCl_2(CO)_2]$ derivative and the attempted carbonylation of $[Pd(\mu\text{-}Cl)Cl(CO)]_2$ (which for the Pt analogue leads to *trans*-$[PtCl_2(CO)_2]$) was also unsuccessful.

---

(1) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York, 1982; Vol. 6, p 280.

(2) Malatesta, L.; Naldini, L. *Gazz. Chim. Ital.* **1960**, *90*, 1505.

(3) Dell'Amico, D. B.; Calderazzo, F. *Gazz. Chim. Ital.* **1979**, *109*, 99.

(4) Dell'Amico, D. B.; Calderazzo, F.; Veracini, C. A.; Zandonã, N. *Inorg. Chem.* **1984**, *23*, 3030.

(5) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

(6) Usón, R.; Forniés, J.; Martínez, F.; Tomás, M.; Reoyo, I. *Organometallics* **1983**, *2*, 1386.

(7) Anal. Calcd for I (Found): C, 40.83 (41.09); H, 2.93 (2.73). Calcd for II (Found): C, 31.65 (32.05); H, 2.57 (2.13). Calcd for III (Found): C: 35.45 (35.67); H, 2.42 (2.37). Calcd for IV (Found): C, 29.44 (28.67); H, 2.21 (1.90). Calcd for V (Found): C, 32.45 (33.86). Calcd for VI (Found): C, 25.14 (25.44). Calcd for VII (Found): C, 28.58 (28.73). Cald for VIII (Found): C, 22.44 (22.43).

(8) These modes are related to the skeletal symmetry of the complexes and behave as ν(M–C) (see ref 9).

(9) Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977; p 437.

(10) Casabó, J.; Coronas, J. M.; Sales, J. *Inorg. Chim. Acta* **1974**, *11*, 5.

(11) Calderazzo, F. Dell'Amico, D. B. *Inorg. Chem.* **1981**, *20*, 1310.

(12) Irving, R. J.; Magnusson, E. A. *J. Chem. Soc.* **1958**, 2283.

(13) Dell'Amico, D. B.; Calderazzo, F.; Zandonã, N. *Inorg. Chem.* **1984**, *23*, 137.

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

Registry No. I, 97877-50-4; II, 97877-51-5; III, 97877-52-6; IV, 97877-53-7; V, 97877-54-8; VI, 97877-55-9; VII, 97877-56-0; VIII, 97877-57-1.

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

Ashraf A. Ismail, Francoise Sauriol, Jacqueline Sedman, and Ian S. Butler*

Department of Chemistry, McGill University
Montreal, Quebec, Canada H3A 2K6

Received April 16, 1985

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.

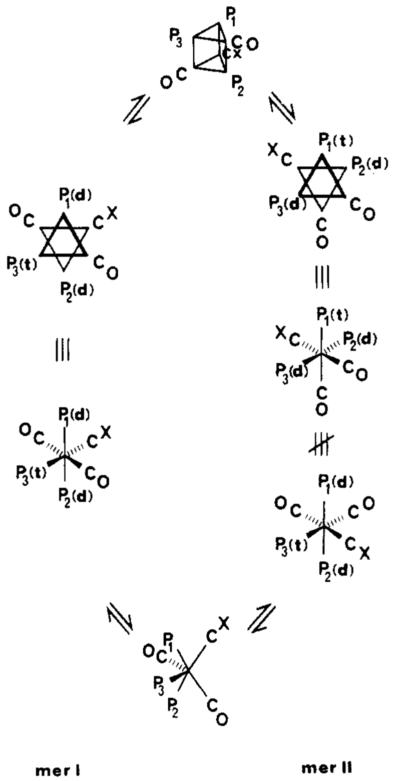
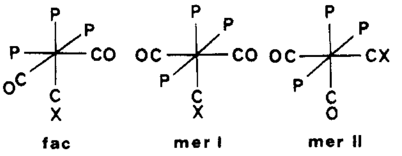


Figure 1. Possible mechanisms for the interconversion of the *mer*-I and *mer*-II $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) isomers. The MeO groups have been omitted for the sake of clarity.



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-

---

(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.