

# 19. Complexes of 3,3'-Oxybis[(diphenylphosphino)methylbenzene] with Ni(II), Pd(II), Pt(II), Rh(I), and Ag(I). How Important is Backbone Rigidity in the Formation of *trans*-Spanning Bidentate Chelates?

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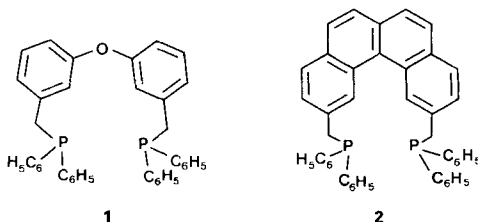
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(29.VIII.86)

The bidentate diphosphine ligand, 3,3'-oxybis[(diphenylphosphino)methylbenzene] (**1**) forms monomeric, *trans*-square-planar complexes  $\text{MX}_2(\textbf{1})$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ , and, in part,  $\text{N}_3^-, \text{NCS}^-, \text{CN}^-, \text{NO}_3^-$ ) as well as  $\text{Pt}(\text{H})\text{Cl}(\textbf{1})$ ,  $\text{Pt}(\text{H})\text{Br}(\textbf{1})$ , and  $\text{RhCl}(\text{CO})(\textbf{1})$ . Polymeric species have been observed with substitutionally inert metal centres: *trans*- $[\text{PtCl}_2(\textbf{1})]_2$  and *cis*- $[\text{PtCl}_2(\textbf{1})]_n$  (mean value of  $n \approx 4-5$ ).  $^{31}\text{P}$ -NMR, and selected IR and UV/VIS parameters are reported. Ligand **1** shows a marked preference for *trans*-spanning and monomeric chelate formation, despite its various degrees of freedom of internal rotation in the ligand backbone. The readily available ligand **1** as well as analogues with other donor atoms, therefore, appear useful in most potential applications of *trans*-spanning chelate ligands. The crystal structure of  $\text{AgCl}(\textbf{1}) \cdot 0.5 (\text{CH}_3)_2\text{C}=\text{O} \cdot 0.39 \text{C}_6\text{H}_{12}$  (space group  $C2/c$ ,  $a = 21.02 \text{ \AA}$ ,  $b = 14.57 \text{ \AA}$ ,  $c = 24.79 \text{ \AA}$ ,  $\beta = 99.77^\circ$ ,  $V = 7531.4 \text{ \AA}^3$ ,  $Z = 8$ ) confirms the presence of three-coordinate  $\text{Ag}(\textbf{1})$ , with a coordination intermediate between a trigonal-planar and a T-shaped geometry ( $\text{P}-\text{Ag}-\text{P} = 145.61(8)^\circ$ ).

**Introduction.** – In recent years, a variety of ligands has been described, which were designed more or less specifically to span *trans*-positions in mononuclear, square planar complexes [1]. The most systematic and extensive attempt in this direction is due to Venanzi and coworkers [2]. The ligand 2,11-bis(diphenylphosphinomethyl)benzo-[c]phenanthrene (**2**) proved to form a great variety of *trans*-spanning chelate complexes. The well-documented preference of **2** for *trans*-square-planar coordination has found



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applications in mechanistic [3] [4] and structural [2] [5] studies. Other work, however, showed that **2**, despite its rigid backbone and the steric hindrance exerted by the four phosphinophenyl groups, did not completely prevent the formation of monomeric *cis*-square planar [6] or six-coordinate species [7]. These observations raise the question, to what extent the well-documented preference for *trans*-spanning chelation of ligand **2** is due to restricted backbone flexibility. We examine here, whether a similar preference is found with the somewhat more flexible ligand **1**. This ligand is much more readily synthesized than **2**.

Ligand **1** has recently been reported to afford *trans*-PtCl<sub>2</sub>(**1**) in 87% yield by reaction with PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> in benzene [8]. This yield is similar to that reported for the reaction: Na<sub>2</sub>PtCl<sub>4</sub> + **2** → *trans*-PtCl<sub>2</sub>(**2**) in acetone (≈ 92%) [9]. Since these results are so similar, a more systematic comparison of the structural preferences between **1** and **2** in complex formation appeared of interest. Our comparison involves nd<sup>8</sup> metal centres with a known preference for square-planar coordination. Among these, the kinetically more labile centres, Ni(II) and Pd(II) provide a measure of the *thermodynamic* preference for *trans*-chelation. In contrast, complex formation involving more inert Pt(II) and Rh(I) could be subject to *kinetic control*. Incomplete specificity for *trans*-chelation (caused by kinetic or thermodynamic factors, or both) is expected to result in the formation of polymeric species or of complexes with alternative coordination geometry.

Formation of *trans*-chelated or other species may require distortion of the unstrained, minimum-energy conformation of the free ligand. A study of conformationally flexible nd<sup>10</sup> complexes can provide a first answer as to the importance of ligand distortion in the formation of these *trans*-spanning chelate complexes. Structural data on three-coordinate AgCl(**1**) are thus included in this study.

**Results.** – *Complexes of Ni(II) and Pd(II).* A series of monomeric compounds of the general formula MX<sub>2</sub>(**1**) has been synthesized by reaction of MX<sub>2</sub> with **1** (Table 1). All isolated compounds were exempt of isomers (<sup>31</sup>P-NMR); a single resonance was observed in all cases (Table 2). Their <sup>1</sup>H-NMR, spectra are consistent with a *trans*-square-planar configuration (Table 2): a deceptively simple triplet pattern for the CH<sub>2</sub> protons was observed. This 'virtual coupling' (|<sup>2</sup>J(P, H) + <sup>4</sup>J(P, H)|) is generally indicative of a *trans*-configuration of two P donors, and this also holds for the analogous complexes of ligand **2** [9].

The lack of paramagnetic shifts and line broadening in the NMR spectra of the Ni(II) complexes is consistent with the absence of tetrahedral species at equilibrium with the *trans*-square-planar form. The UV/VIS spectra of some of the Ni(II) species (Table 3) corroborate this conclusion. They closely resemble the spectra of analogous species with ligand **2**, except that the UV region is not dominated to as high wavelengths by ligand π → π\* absorptions [9]<sup>3)</sup>.

The IR spectra of the complexes of **1** are also less dominated by ligand bands compared with complexes of **2**. Polyatomic ligands X in MX<sub>2</sub>(**1**) give rise to strong, characteristic IR bands:  $\tilde{\nu}(\text{C}\equiv\text{N})$  at 2110 cm<sup>-1</sup> in Ni(CN)<sub>2</sub>(**1**),  $\tilde{\nu}(\text{C}\equiv\text{N})$  at 2080 cm<sup>-1</sup> in Ni(NCS)<sub>2</sub>(**1**), characteristic of N-bonded thiocyanate ( $\tilde{\nu}(\text{C}\equiv\text{N}) = 2086$  cm<sup>-1</sup> in Ni(NCS)<sub>2</sub>(**2**) [9]),  $\tilde{\nu}(\text{N}\equiv\text{N})$  at 2023 and 2040 cm<sup>-1</sup> (KBr and crystalline film preparations)

<sup>3)</sup> The complexes of **1** are, therefore, better suited to kinetic studies by UV spectrophotometry.

Table 1. Analytical Data for Complexes of Ligand 1

| Compounds                                                                                     | Color        | C [%] |       | H [%] |       | Other elements [%]  |                                 | Mol.-wt. (CH <sub>2</sub> Cl <sub>2</sub> ) |       |
|-----------------------------------------------------------------------------------------------|--------------|-------|-------|-------|-------|---------------------|---------------------------------|---------------------------------------------|-------|
|                                                                                               |              | Calc. | Found | Calc. | Found | Calc.               | Found                           | Calc.                                       | Found |
| <i>trans</i> -NiCl <sub>2</sub> (1)                                                           | red          | 65.55 | 65.71 | 4.63  | 4.75  | Ni 8.43<br>Cl 10.18 | (8.19 ± 0.08)<br>(10.55 ± 0.11) | 696                                         | 691   |
| <i>trans</i> -NiCl <sub>2</sub> (1)                                                           | purple       | 58.13 | 58.21 | 4.11  | 4.19  | Ni 7.48             | (7.24 ± 0.07)                   | 785                                         | 780   |
| <i>trans</i> -NiI <sub>2</sub> (1)                                                            | black-green  | 51.91 | 51.94 | 3.67  | 3.74  | Br 20.35<br>Ni 6.68 | (20.87 ± 0.20)<br>(6.48 ± 0.15) | 879                                         | 870   |
| <i>trans</i> -Ni(NCS) <sub>2</sub> (1)                                                        | orange       | 64.79 | 64.78 | 4.35  | 4.40  | I 28.87<br>Ni 7.92  | (29.48 ± 0.30)<br>(7.59 ± 0.10) |                                             |       |
| <i>trans</i> -Ni(CN) <sub>2</sub> (1)                                                         | yellow       | 70.93 | 71.10 | 4.76  | 4.82  | N 3.78<br>Ni 8.67   | 3.70<br>(8.66 ± 0.12)           | 677                                         | 678   |
| <i>trans</i> -PdCl <sub>2</sub> (1)                                                           | yellow       | 61.32 | 61.42 | 4.32  | 4.38  |                     |                                 |                                             |       |
| <i>trans</i> -PdBr <sub>2</sub> (1)                                                           | orange       | 54.78 | 55.21 | 3.87  | 3.94  |                     |                                 |                                             |       |
| <i>trans</i> -PdI <sub>2</sub> (1)                                                            | orange-brown | 49.22 | 49.19 | 3.48  | 3.56  |                     |                                 | 926                                         | 915   |
| <i>trans</i> -Pd(ONO <sub>2</sub> ) <sub>2</sub> (1)                                          | yellow       | 57.27 | 57.24 | 4.05  | 4.31  | N 3.52              | 3.68                            |                                             |       |
| <i>trans</i> -Pd(N <sub>3</sub> ) <sub>2</sub> (1)                                            | yellow       | 60.29 | 60.16 | 4.26  | 4.18  | N 11.10             | 11.19                           | 757                                         | 758   |
| <i>trans</i> -PtBr <sub>2</sub> (1)                                                           | yellow       | 49.52 | 49.54 | 3.56  | 3.58  |                     |                                 | 922                                         | 930   |
| <i>trans</i> -PtI <sub>2</sub> (1)                                                            | orange       | 44.95 | 44.50 | 3.18  | 3.24  |                     |                                 |                                             |       |
| <i>trans</i> -PtHCl(1)                                                                        | white        | 57.18 | 56.98 | 4.16  | 4.13  | Cl 4.45             | 4.39                            |                                             |       |
| <i>trans</i> -PtHBr(1)                                                                        | white        | 54.17 | 54.36 | 3.94  | 3.88  | Br 9.48             | 9.57                            |                                             |       |
| <i>trans</i> -RhCl(CO)(1)                                                                     | yellow       | 63.90 | 63.85 | 4.40  | 4.49  |                     |                                 | 733                                         | 735   |
| AgCl(1)·0.5(CH <sub>3</sub> ) <sub>2</sub> CO·0.5C <sub>6</sub> H <sub>12</sub> <sup>a)</sup> | colourless   | 64.04 | 64.97 | 5.18  | 4.54  |                     |                                 | 770                                         | 762   |

<sup>a)</sup> See discussion of stoichiometry in crystallographic section of the *Exper. Part*.

Table 2.  $^{31}\text{P}$ - and  $^1\text{H}$ -NMR Parameters of **1** and its Derivatives in  $\text{CDCl}_3$ 

| Compound                                                                                                        | $^{31}\text{P}$ -NMR |                                 | $^1\text{H}$ -NMR ( $\delta$ [ppm], $J$ [Hz]) |                                       |                                       |                                                                           |                                    |
|-----------------------------------------------------------------------------------------------------------------|----------------------|---------------------------------|-----------------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------------------------------------------|------------------------------------|
|                                                                                                                 | $\delta$ [ppm]       | $^1J(\text{Pt}, \text{P})$ [Hz] | $\delta(\text{H}_\text{A})^\text{a)}$         | $\delta(\text{H}_\text{B})^\text{a)}$ | $\delta(\text{H}_\text{C})^\text{a)}$ | $^2J(\text{P}, \text{H}_\text{C})$<br>$+^4J(\text{P}, \text{H}_\text{C})$ | $^3J(\text{M}, \text{H}_\text{C})$ |
| ( <b>1</b> ) <sup>b)</sup>                                                                                      | –9.65                | –                               | °)                                            | °)                                    | 3.22                                  | –                                                                         | –                                  |
| ( <b>1</b> )dioxide                                                                                             | 28.99                | –                               | °)                                            | °)                                    | 3.59                                  | d)                                                                        | –                                  |
| <i>trans</i> -NiCl <sub>2</sub> ( <b>1</b> )                                                                    | 6.51                 | –                               | 9.33                                          | 6.14                                  | 3.57                                  | 10.3                                                                      | –                                  |
| <i>trans</i> -NiBr <sub>2</sub> ( <b>1</b> )                                                                    | 14.03                | –                               | 9.33                                          | 6.13                                  | 3.85                                  | 10.0                                                                      | –                                  |
| <i>trans</i> -NiI <sub>2</sub> ( <b>1</b> )                                                                     | 29.31                | –                               | 9.12                                          | 6.03                                  | 4.27                                  | 8.8                                                                       | –                                  |
| <i>trans</i> -Ni(NCS) <sub>2</sub> ( <b>1</b> )                                                                 | 12.83                | –                               | 8.70                                          | 6.14                                  | 3.49                                  | 8.8                                                                       | –                                  |
| <i>trans</i> -Ni(CN) <sub>2</sub> ( <b>1</b> )                                                                  | 24.85                | –                               | 8.31                                          | 6.07                                  | 4.96                                  | 9.1                                                                       | –                                  |
| <i>trans</i> -PdCl <sub>2</sub> ( <b>1</b> )                                                                    | 20.10                | –                               | 8.44                                          | 6.19                                  | 3.88                                  | 8.5                                                                       | –                                  |
| <i>trans</i> -PdBr <sub>2</sub> ( <b>1</b> )                                                                    | 17.17                | –                               | 8.49                                          | 6.24                                  | 4.12                                  | 8.5                                                                       | –                                  |
| <i>trans</i> -PdI <sub>2</sub> ( <b>1</b> )                                                                     | 7.24                 | –                               | 8.46                                          | 6.23                                  | 4.49                                  | 8.2                                                                       | –                                  |
| <i>trans</i> -Pd(NO <sub>3</sub> ) <sub>2</sub> ( <b>1</b> )                                                    | 14.23                | –                               | –                                             | –                                     | –                                     | –                                                                         | –                                  |
| <i>trans</i> -Pd(N <sub>3</sub> ) <sub>2</sub> ( <b>1</b> )                                                     | 19.10                | –                               | 7.99                                          | 6.16                                  | 3.68                                  | 8.2                                                                       | –                                  |
| <i>trans</i> -PtCl <sub>2</sub> ( <b>1</b> )                                                                    | 16.45                | 2605                            | 8.49                                          | 6.27                                  | 3.93                                  | 8.8                                                                       | 28.2                               |
| <i>trans</i> -[PtCl <sub>2</sub> ( <b>1</b> )] <sub>2</sub>                                                     | 15.28                | 2573                            | °)                                            | °)                                    | ≈ 4.0                                 | ≈ 9                                                                       | ≈ 30                               |
| <i>cis</i> -PtCl <sub>2</sub> ( <b>1</b> )                                                                      | 9.77                 | 3678                            | 8.30                                          | °)                                    | 4.87–3.55                             | f)                                                                        | g)                                 |
| <i>cis</i> -[PtCl <sub>2</sub> ( <b>1</b> )]                                                                    | 8.85–9.43            | 3677–3727                       | °)                                            | °)                                    | 4.0–4.3                               | h)                                                                        | h)                                 |
|                                                                                                                 |                      |                                 |                                               |                                       | (broad)                               |                                                                           |                                    |
| <i>trans</i> -PtBr <sub>2</sub> ( <b>1</b> )                                                                    | 13.09                | 2521                            | 8.56                                          | 6.32                                  | 4.15                                  | 8.8                                                                       | 28.8                               |
| <i>trans</i> -PtI <sub>2</sub> ( <b>1</b> )                                                                     | 4.74                 | 2451                            | 8.80                                          | 6.33                                  | 4.50                                  | 8.2                                                                       | 30.2                               |
| <i>trans</i> -PtHCl( <b>1</b> )                                                                                 | 25.55 <sup>b)</sup>  | 2969                            | 8.52                                          | 6.07                                  | 3.86                                  | 7.5                                                                       | 37.8 <sup>i)</sup>                 |
| <i>trans</i> -PtHBr( <b>1</b> )                                                                                 | 25.16 <sup>b)</sup>  | 2975                            | 8.47                                          | 6.10                                  | 3.92                                  | 7.5                                                                       | 37.3 <sup>k)</sup>                 |
| <i>trans</i> -RhCl(CO)( <b>1</b> )                                                                              | 26.42                | 126                             | 8.28                                          | 6.34                                  | 4.30/3.50 <sup>l)</sup>               | 8                                                                         | m)                                 |
| AgCl( <b>1</b> ) · 0.5(CH <sub>3</sub> ) <sub>2</sub> CO · 0.5C <sub>6</sub> H <sub>12</sub> ≈ 13 <sup>b)</sup> |                      | ≈ 420 <sup>n)</sup>             | °)                                            | 6.25                                  | 3.65                                  | 6.7                                                                       |                                    |

a)

b) Solvent C<sub>6</sub>D<sub>6</sub>.

c) Protons not identified.

d)  $^2J(\text{P}, \text{H}) = 13.5$  Hz.

e) Other aromatic protons: 7.8–8.2 and 6.17–7.7 ppm.

f)  $^2J(\text{H}, \text{H}') = 14$  Hz;  $^2J(\text{H}, \text{P}) = 12$  Hz.

g) Pt satellites not observed.

h) Coupling not determined (broad lines).

i) Pt–H proton:  $\delta = -15.90$  ppm;  $^2J_{\text{P-HPt}} = 27.4$  Hz;  $^1J_{\text{Pt-H}} = 1200.0$  Hz.

k) Pt–H proton:  $\delta = -14.47$  ppm;  $^2J_{\text{P-HPt}} = 25.3$  Hz;  $^1J_{\text{Pt-H}} = 1255.0$  Hz.

l) Two signals due to sets of two inequivalent CH<sub>2</sub> protons.

m)  $^2J(\text{H}, \text{H}) = 13$  Hz.

n) Broadened lines at 298 K;  $^1J(^{107}\text{Ag}, ^{31}\text{P})$  and  $^1J(^{109}\text{Ag}, ^{31}\text{P})$  not resolved.

Table 3. UV/VIS Spectra of Complexes with **1** in  $\text{CH}_2\text{Cl}_2$ ,  $T = 20^\circ$ 

| Complex                                      | Spectral Parameters <sup>a)</sup> $\lambda$ [nm], ( $\epsilon$ [l · mol <sup>–1</sup> · cm <sup>–1</sup> ])                                                                   |
|----------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| NiCl <sub>2</sub> ( <b>1</b> )               | 494 (421), max; 437 (215), min; 379 (15400), max; 332 (1210), min; 290 (7970), sh; 275 (11800), sh; 266 (13300), max; 262 (13200), min; 245 (27600), sh.                      |
| NiBr <sub>2</sub> ( <b>1</b> ) <sup>b)</sup> | 549 (428), max; 468 (233), min; 405 (8630), max; 368 (2090), min; 326 (5480), sh; 296 (8030), sh; 267 (19900), sh; 251 (30100), max; 243 (29100), min.                        |
| NiI <sub>2</sub> ( <b>1</b> ) <sup>b)</sup>  | 617 (509), max; 556 (405), min; 400 (4500), sh; 345 (7660), max; 334 (7610), min; 298 (19600), max; 273 (14400), min; 260 (24500), sh.                                        |
| Ni(NCS) <sub>2</sub> ( <b>1</b> )            | 500 (711), sh; 394 (9760), max; 453 (2250), min; 312 (22000), max; 293 (11400), min; 285 (11900), max; 280 (11700), min; 275 (11900), max; 269 (10900), min; 247 (28900), sh. |
| Ni(CN) <sub>2</sub> ( <b>1</b> )             | 350 (931), sh; 312 (9850), sh; 295 (16000), max; 289 (15600), min; 275 (30400), max; 260 (19200), sh; 253 (18200), min.                                                       |
| PdCl <sub>2</sub> ( <b>1</b> )               | 335 (18800), max; 298 (4320), min; 287 (6470), sh; 274 (9250), max; 266 (8680), sh; 263 (8510), min.                                                                          |

Table 3 (cont.)

| Complex                                | Spectral Parameters <sup>a)</sup> $\lambda$ [nm], ( $\epsilon$ [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ])     |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| $\text{PdBr}_2(\mathbf{1})^b$          | 358 (12 100), max; 332 (5460), min; 306 (10 500), max; 292 (9480), sh; 282 (8450), min; 275 (9590), sh.                       |
| $\text{PdI}_2(\mathbf{1})^b$           | 421 (3320), max; 396 (2560), min; 327 (13 900), max; 302 (9750), min; 292 (12 000), sh; 270 (20 100), max; 264 (20 000), min. |
| $\text{PtCl}(\mathbf{1})^c$            | 315 (846), sh; 275 (19 800), max; 263 (15 700), min.                                                                          |
| $\text{PtBr}_2(\mathbf{1})$            | 342 (554), sh; 290 (11 100), max; 282 (9630), min; 275 (10 300), sh.                                                          |
| $\text{PtI}_2(\mathbf{1})$             | 348 (2510), max; 335 (2380), min; 301 (7080), sh; 272 (16 600), sh.                                                           |
| $\text{RhCl}(\text{CO})(\mathbf{1})^c$ | 363 (3390), max; 328 (1410), min; 274 (14 000), max; 270 (13 800), min.                                                       |

<sup>a)</sup> Accuracy in  $\lambda$ :  $\pm 1.5$  nm; accuracy in  $\epsilon$   $\pm 5\%$ .  
<sup>b)</sup> Spectral stability checked: spectrum remained unchanged for 30 min.  
<sup>c)</sup> *trans*-Monomer.

in  $\text{Pd}(\text{N}_3)_2(\mathbf{1})$ , indicative of two inequivalent  $\text{N}_3^-$  sites in the crystal<sup>4)</sup>, and frequencies characteristic of unidentate  $\text{NO}_3^-$  at 1510, 1388, 1275, 1255, and 955  $\text{cm}^{-1}$  in  $\text{Pd}(\text{NO}_3)_2(\mathbf{1})$ .

Single  $\tilde{\nu}(\text{M}-\text{Cl})$  frequencies were identified at 408  $\text{cm}^{-1}$  in *trans*- $\text{NiCl}_2(\mathbf{1})$  and 360  $\text{cm}^{-1}$  in *trans*- $\text{PdCl}_2(\mathbf{1})$ . The  $\tilde{\nu}(\text{Ni}-\text{Br})$  frequency was found at 326  $\text{cm}^{-1}$  in *trans*- $\text{NiBr}_2(\mathbf{1})$ . These assignments are supported by comparison with their iodo analogues.

*Complexes of Rh(I) and Pt(II).* For these two metal centres, more than one product was obtained in several synthetic procedures. Thus, reaction of  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$  with  $\mathbf{1}$  in benzene gave a  $\text{CH}_3\text{CN}$ -soluble and an insoluble fraction. The soluble fraction was homogeneous on the basis of its  $^{31}\text{P}$ -NMR spectrum. Elemental analysis and vapour-pressure osmometry established it to be monomeric  $\text{RhCl}(\text{CO})(\mathbf{1})$ . Its  $^1\text{H}$ -NMR spectrum shows two signals for the  $\text{CH}_2$  protons, each appearing as a 'virtual coupling' triplet. As observed previously for *trans*- $\text{RhCl}(\text{CO})(\mathbf{2})$  [7], these protons are pairwise inequivalent as

Table 4. Starting Materials and Reaction Conditions in the Synthesis of  $\text{PtCl}_2(\mathbf{1})$ 

| Exper. No. | Starting Pt compound                             | Solvent, concentration                                  | Reaction conditions                        | Appr. yields of products [%]               |                                                |                                              |
|------------|--------------------------------------------------|---------------------------------------------------------|--------------------------------------------|--------------------------------------------|------------------------------------------------|----------------------------------------------|
|            |                                                  |                                                         |                                            | <i>trans</i> - $\text{PtCl}_2(\mathbf{1})$ | <i>trans</i> - $[\text{PtCl}_2(\mathbf{1})]_2$ | <i>cis</i> - $[\text{PtCl}_2(\mathbf{1})]_n$ |
| 1          | $\text{PtCl}_2(\text{CH}_3\text{CN})_2$          | toluene/MeCN (100:1), $2.8 \times 10^{-2} \text{ M}$    | 80° (2 h), then 100° (2 h)                 | 87 <sup>a)</sup>                           | $\approx 10^b$ <sup>c)</sup>                   | $< 5^b$ <sup>c)</sup>                        |
| 2          | $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | MeCN, $1.7 \times 10^{-2} \text{ M}$                    | 1 h $\uparrow\downarrow$ , then 12 h, r.t. | 70 <sup>b)</sup>                           | 12 <sup>b)</sup>                               | 13 <sup>b)</sup>                             |
| 3          | $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | MeCN, $5.8 \times 10^{-3} \text{ M}$                    | 12 h $\uparrow\downarrow$                  | 60 <sup>a)</sup>                           | $\approx 10^b$ <sup>c)</sup>                   | $\approx 5^a$                                |
| 4          | $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | $\text{C}_6\text{H}_6$ , $1.7 \times 10^{-2} \text{ M}$ | 1 h $\uparrow\downarrow$                   | 40 <sup>b)</sup>                           | 55 <sup>b)</sup>                               | 5 <sup>b)</sup>                              |
| 5          | $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | $\text{C}_6\text{H}_6$ , $9.3 \times 10^{-2} \text{ M}$ | 2 h $\uparrow\downarrow$ , then 12 h, r.t. | 71 <sup>a)</sup>                           | <sup>d)</sup>                                  | 14 <sup>a)</sup>                             |
| 6          | $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ | $\text{C}_6\text{H}_6$ , $3.2 \times 10^{-3} \text{ M}$ | 12 h, r.t.                                 | 50 <sup>a)</sup>                           | <sup>d)</sup>                                  | 12 <sup>a)</sup>                             |
| 7          | $\text{K}_2\text{PtCl}_4$                        | HCl, 10M $3.3 \times 10^{-3} \text{ M}$                 | 12 h $\uparrow\downarrow$                  | 20 <sup>b)</sup>                           | $< 2^b$                                        | 80 <sup>b)</sup>                             |
| 8          | $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ | $\text{C}_6\text{H}_6$ , $4.2 \times 10^{-3} \text{ M}$ | 1 h, r.t.; then 1 h $\uparrow\downarrow$   | 55                                         | 45                                             | 2                                            |

<sup>a)</sup> Isolated yield; for *trans*- $\text{PtCl}_2(\mathbf{1})$ : isolated product after chromatography.

<sup>b)</sup> From  $^{31}\text{P}$ -NMR integral; error  $\pm 10\%$  rel.

<sup>c)</sup> By  $^{31}\text{P}$ -NMR integral on mother liquor.

<sup>d)</sup> Not determined.

<sup>4)</sup> The NMR spectra are consistent with one solution species with equivalent  $\text{N}_3^-$  ligands (see below).

a consequence of the *trans*-position of the two different ligands, Cl and CO. The insoluble fraction of the Rh complex had an IR spectrum almost identical with that of the *trans*-monomer ( $\tilde{\nu}(\text{C}\equiv\text{O}) = 1940\text{ cm}^{-1}$ ), but owing to its insolubility, this presumed polymer,  $[\text{RhCl}(\text{CO})(\mathbf{1})]_x$ , could not be characterized by solution NMR spectroscopy.

The nature of the different Pt complexes formed by the different synthetic procedures (Table 4) as well as their relative quantities depend strongly on the nature of the starting material and solvent. The reaction stoichiometry, reaction time, and temperature also affect the yields of the different products. Apart from yellow, monomeric *trans*- $\text{PtCl}_2(\mathbf{1})$  [8] (which was recovered quantitatively by chromatography), both *trans*- and *cis*-polymers were identified in solution. The  $^{31}\text{P}$ -NMR spectrum of the *trans*-monomer shows a  $J(\text{Pt}, \text{P})$  value characteristic of a *trans*-configuration. Its  $^1\text{H}$ -NMR spectrum also shows a 'virtual coupling' triplet of the  $\text{CH}_2$  protons (with the corresponding  $^{195}\text{Pt}$  satellites), characteristic of a *trans*-compound.

Reaction of Zeise's dimer  $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$  or of  $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$  in benzene for short reaction times gave good yields of a second yellow species which proved to be a dimer from a molecular-mass determination. Its  $^{31}\text{P}$ -NMR spectrum as well as the  $\text{CH}_2$  region of the poorly resolved  $^1\text{H}$ -NMR spectrum appeared similar to those of the *trans*-monomer. However, the aromatic proton pattern is different (see Table 2).

All, except the above two preparative procedures afforded variable amounts of a white, non-crystalline, and only partly soluble material. The soluble fraction of this material was a mixture of species with a mean molecular mass corresponding to that of a tetramer or pentamer. The mean molecular mass was found to vary for different isolation procedures. Its  $^{31}\text{P}$ -NMR spectrum shows several broad peaks. The coupling constants as well as the  $^{31}\text{P}$  chemical shifts are very similar, consistent with a mixture of homologous polymers; their values are characteristic of a *cis*- $\text{PtP}_2\text{Cl}_2$  central coordination unit. These chemical shifts and coupling constants are close to those of authentic, monomeric *cis*- $\text{PtCl}_2(\mathbf{1})$  prepared by an alternative route [8] [10]. The  $^1\text{H}$ -NMR spectrum of these mixtures of polymers are poorly resolved, but the  $\text{CH}_2$  pattern was nevertheless seen to be a doublet-like pattern. The IR spectrum of the *cis*-polymer mixtures shows two  $\tilde{\nu}(\text{Pt}-\text{Cl})$  bands at 290 and 320  $\text{cm}^{-1}$ , whereas the *trans*-monomer shows only one, at 343  $\text{cm}^{-1}$  [8].

Both *cis*- and *trans*-polymers were found to be rather unstable in solution, isomerizing in part into *trans*-monomer and other polymers. This precluded their more detailed investigation in solution. On the other hand, it was attempted to isomerize them by thermal reaction in different solvents or in the presence of free ligand. No *cis*-monomer was formed in detectable amounts in these experiments.

Finally, no insoluble products were obtained in the preparation of *trans*- $\text{PtBr}_2(\mathbf{1})$  and *trans*- $\text{PtI}_2(\mathbf{1})$  from  $\text{PtBr}_2$  and  $\text{PtI}_2$ , respectively, in MeCN;  $\lesssim 5\%$  of other species ( $^{31}\text{P}$ -NMR spectra of the crude isolated compounds), including polymers, were formed.

The hydrido complexes  $\text{Pt}(\text{H})\text{Cl}(\mathbf{1})$  and  $\text{Pt}(\text{H})\text{Br}(\mathbf{1})$  were obtained, by ligand exchange, from their *trans*-bis(triphenylphosphine) analogues, with retention of configuration. The ligand  $\mathbf{1}$ , thus, reacts in the same way as  $\mathbf{2}$  under these conditions [1] [12].

$\text{AgCl}(\mathbf{1})$ . This complex was obtained by reacting silver chloride with  $\mathbf{1}$  in MeCN. The  $^1\text{H}$ -NMR spectrum of  $\text{AgCl}(\mathbf{1})$  shows a triplet-like pattern for the  $\text{CH}_2$  protons, and the integral confirmed the presence of close to  $\frac{1}{2}$  molecule of the solvents used in the crystallization, viz. acetone and cyclohexane. At ambient temperature, the  $^{31}\text{P}$ -NMR spectrum shows two exchange-broadened signals. The two coupling constants,

$|^1J(^{107}\text{Ag}, ^{31}\text{P})|$  and  $|^1J(^{109}\text{Ag}, ^{31}\text{P})|$  could not be determined at this temperature. However, a rough estimate of the mean value of the two constants, *viz.*  $\sim 420$  Hz could be made. These parameters and the general spectral features are similar to those reported for  $\text{AgCl}(\mathbf{2})$  [13], and a similar structure is inferred for these two compounds in solution. Although the exchange-broadening mechanism has not been studied in  $\text{AgCl}(\mathbf{1})$ , it is likely to be very similar to the known mechanism [13] in  $\text{AgCl}(\mathbf{2})$ , given the close spectral and structural similarities between the two compounds.

The molecular structure of  $\text{AgCl}(\mathbf{1}) \cdot 0.5 (\text{CH}_3)_2\text{C}=\text{O} \cdot 0.39 \text{C}_6\text{H}_{12}$  (*Fig.*, *Tables 5 and 6*) strongly resembles that of  $\text{AgCl}(\mathbf{2})$  [5]. (Distances and angles for the latter compound in

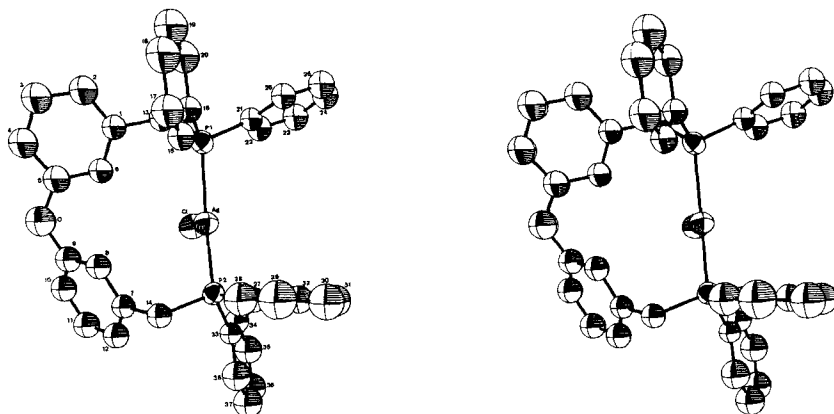


Figure. ORTEP [29] plot of the molecule  $\text{AgCl}(\mathbf{1})$  with atom-numbering scheme

Table 5. Crystal Data and Parameters of Data Collection for  $\text{AgCl}(\mathbf{1})$

|                                                                                                                 |                                                                            |
|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Formula $\text{AgCl}(\mathbf{1}) \cdot 0.5 (\text{CH}_3)_2\text{C}=\text{O} \cdot 0.39 \text{C}_6\text{H}_{12}$ | $\text{C}_{41.8}\text{H}_{39.7}\text{O}_{1.5}\text{P}_2\text{AgCl}$        |
| Formula wt.                                                                                                     | 771.31                                                                     |
| Crystal system and space group                                                                                  | monoclinic, $C2/c$                                                         |
| $a$ [Å]                                                                                                         | 21.02                                                                      |
| $b$ [Å]                                                                                                         | 14.57                                                                      |
| $c$ [Å]                                                                                                         | 24.79                                                                      |
| $\beta$ [°]                                                                                                     | 99.77                                                                      |
| $V$ [Å <sup>3</sup> ]                                                                                           | 7482                                                                       |
| $Z$                                                                                                             | 8                                                                          |
| $d_{\text{calc}}$ [gcm <sup>-3</sup> ]                                                                          | 1.371                                                                      |
| $d_{\text{exp}}$ [gcm <sup>-3</sup> ]                                                                           | 1.38                                                                       |
| $\theta$                                                                                                        | 23°                                                                        |
| Scan method, range                                                                                              | $\omega$ -scan, 1.24°                                                      |
| Scan rate                                                                                                       | 1 s/0.02° for $\theta < 15^\circ$ , 2s/0.02° for $\theta > 15^\circ$       |
| Radiation                                                                                                       | $\text{MoK}_\alpha (\lambda = 0.71069 \text{ Å})$ , graphite monochromated |
| No. of unique reflections                                                                                       | 5240                                                                       |
| No. of reflections ( $F_o > 3\sigma(F_o)$ )/no. of variables                                                    | 3811/219                                                                   |
| Absorption coefficient, $\mu$                                                                                   | 6.17 cm <sup>-1</sup>                                                      |
| Refinement method                                                                                               | block-matrix least-squares                                                 |
| Weighting system                                                                                                | unit weight                                                                |
| $R/R_w$                                                                                                         | 0.062/0.063                                                                |
| Goodness of fit                                                                                                 | 1.56                                                                       |
| Extinction factor [28]                                                                                          | 0.00543(2)                                                                 |

Table 6. *Final Positional and Equivalent Isotropic Thermal Parameters for Non-H-Atoms with e.s.d. of Last Significant Digit in Parentheses*

| Atom  | <i>x/a</i>  | <i>y/b</i>  | <i>z/c</i>  | $U_{\text{iso}}[\text{\AA}]^2$ |
|-------|-------------|-------------|-------------|--------------------------------|
| Ag    | 0.19616(3)  | 0.24014(4)  | 0.26020(3)  | 0.0566(4) <sup>a)</sup>        |
| Cl    | 0.24435(13) | 0.08187(16) | 0.25244(10) | 0.0565(16) <sup>a)</sup>       |
| P(1)  | 0.21341(10) | 0.24903(15) | 0.35971(8)  | 0.0485(13) <sup>a)</sup>       |
| P(2)  | 0.15953(10) | 0.32025(14) | 0.17605(9)  | 0.0469(13) <sup>a)</sup>       |
| O(1)  | 0.4312(4)   | 0.3121(5)   | 0.2683(3)   | 0.0841(20)                     |
| C(1)  | 0.3474(4)   | 0.2494(6)   | 0.3804(4)   | 0.0553(21)                     |
| C(2)  | 0.3845(5)   | 0.2967(7)   | 0.4226(4)   | 0.0711(27)                     |
| C(3)  | 0.4370(5)   | 0.3477(7)   | 0.4129(5)   | 0.0773(29)                     |
| C(4)  | 0.4506(5)   | 0.3540(7)   | 0.3616(4)   | 0.0727(27)                     |
| C(5)  | 0.4127(5)   | 0.3073(7)   | 0.3191(4)   | 0.0664(25)                     |
| C(6)  | 0.3614(4)   | 0.2536(6)   | 0.3284(4)   | 0.0562(21)                     |
| C(7)  | 0.2869(4)   | 0.3452(6)   | 0.1630(4)   | 0.0522(21)                     |
| C(8)  | 0.3277(4)   | 0.3508(6)   | 0.2129(4)   | 0.0571(22)                     |
| C(9)  | 0.3871(5)   | 0.3039(7)   | 0.2202(4)   | 0.0625(24)                     |
| C(10) | 0.4054(5)   | 0.2544(7)   | 0.1793(4)   | 0.0675(24)                     |
| C(11) | 0.3656(5)   | 0.2497(7)   | 0.1304(4)   | 0.0724(26)                     |
| C(12) | 0.3061(5)   | 0.2942(7)   | 0.1208(4)   | 0.0656(25)                     |
| C(13) | 0.2898(4)   | 0.1942(6)   | 0.3910(4)   | 0.0576(22)                     |
| C(14) | 0.2222(4)   | 0.3935(6)   | 0.1553(4)   | 0.0548(22)                     |
| C(15) | 0.2153(4)   | 0.3600(6)   | 0.3932(4)   | 0.0515(21)                     |
| C(16) | 0.2069(4)   | 0.4380(6)   | 0.3608(4)   | 0.0564(22)                     |
| C(17) | 0.2098(5)   | 0.5243(7)   | 0.3841(4)   | 0.0714(27)                     |
| C(18) | 0.2204(5)   | 0.5326(7)   | 0.4394(5)   | 0.0778(29)                     |
| C(19) | 0.2302(5)   | 0.4569(8)   | 0.4730(5)   | 0.0822(30)                     |
| C(20) | 0.2273(5)   | 0.3703(7)   | 0.4497(5)   | 0.0722(27)                     |
| C(21) | 0.1541(4)   | 0.1803(6)   | 0.3873(4)   | 0.0489(20)                     |
| C(22) | 0.1536(5)   | 0.0864(7)   | 0.3795(4)   | 0.0648(25)                     |
| C(23) | 0.1049(5)   | 0.0320(7)   | 0.3945(4)   | 0.0738(28)                     |
| C(24) | 0.0577(5)   | 0.0715(7)   | 0.4189(4)   | 0.0723(27)                     |
| C(25) | 0.0573(5)   | 0.1635(7)   | 0.4269(4)   | 0.0693(26)                     |
| C(26) | 0.1054(4)   | 0.2187(6)   | 0.4117(4)   | 0.0582(23)                     |
| C(27) | 0.0897(4)   | 0.3943(6)   | 0.1734(4)   | 0.0534(21)                     |
| C(28) | 0.0950(6)   | 0.4868(8)   | 0.1815(5)   | 0.0877(33)                     |
| C(29) | 0.0400(7)   | 0.5395(10)  | 0.1845(5)   | 0.1110(41)                     |
| C(30) | −0.0197(6)  | 0.4989(9)   | 0.1787(5)   | 0.0979(36)                     |
| C(31) | −0.0250(5)  | 0.4077(8)   | 0.1730(5)   | 0.0819(30)                     |
| C(32) | 0.0297(5)   | 0.3547(7)   | 0.1706(4)   | 0.0683(26)                     |
| C(33) | 0.1379(4)   | 0.2426(6)   | 0.1180(3)   | 0.0505(19)                     |
| C(34) | 0.1435(5)   | 0.1502(7)   | 0.1254(4)   | 0.0664(25)                     |
| C(35) | 0.1272(6)   | 0.0904(9)   | 0.0791(5)   | 0.0938(35)                     |
| C(36) | 0.1080(6)   | 0.1277(8)   | 0.0301(5)   | 0.0894(33)                     |
| C(37) | 0.1012(6)   | 0.2157(9)   | 0.0217(5)   | 0.0947(35)                     |
| C(38) | 0.1162(6)   | 0.2779(8)   | 0.0659(5)   | 0.0855(31)                     |
| C(39) | 0.0343(7)   | 0.1170(11)  | 0.2485(7)   | 0.1348(52)                     |
| C(40) | 0.0582(12)  | 0.0362(17)  | 0.2373(10)  | 0.0980(72)                     |
| O(2)  | 0.0562(8)   | 0.1881(12)  | 0.2641(7)   | 0.1088(52)                     |
| C(42) | 0.4490(10)  | 0.0303(14)  | 0.0286(8)   | 0.1368(67)                     |
| C(43) | 0.5116(12)  | 0.0820(18)  | 0.0314(10)  | 0.1828(94)                     |
| C(44) | 0.5520(12)  | 0.0534(18)  | 0.0044(10)  | 0.1828(95)                     |

<sup>a)</sup>  $U_{\text{iso}} = \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$  for Ag, Cl, P(1), and P(2).

parentheses.) Thus, the Ag-atom is three-coordinate, with Ag–Cl = 2.539(3) Å (2.512(1) Å), Ag–P(1) = 2.435(3) Å (2.451(1) Å), Ag–P(2) = 2.400(3) Å (2.412(1) Å). The distance Ag...O(2) (acetone molecule) > 6 Å is clearly nonbonding.

The AgP<sub>2</sub>Cl central coordination unit is almost planar with deviations < 0.013 Å for the donor atoms and –0.032 Å for the Ag atom from the best plane through the four atoms. The arrangement of the donor atoms is intermediate between a trigonal-planar (P(1)–Ag–P(2) = 120°) and a T-shaped geometry (P(1)–Ag–P(2) = 180°, each Cl–Ag–P = 90°). The experimental value for P(1)–Ag–P(2) is 145.61(8)° (140.7(1)°). The coordination in AgCl(**1**) is, thus, somewhat closer to a T-shaped geometry, and this correlates with the Ag–Cl bond length which is 0.027(4) Å longer in AgCl(**1**) than in AgCl(**2**). The conformation of **1** in AgCl(**1**) is analogous to that of ligand **2** in AgCl(**2**). The distances and angles within the chelate ligand are normal.

**Discussion.** – The results of this study establish that the coordination chemistry of **1** and **2** is very similar. For both ligands, monomeric Ni(II) and Pd(II) *trans*-chelates are the only detectable products. Hence, both ligands show a distinct preference for *trans*-chelation. In particular, tetrahedral Ni(II) species were not formed in appreciable amounts with the two ligands. Similar, flexible diphosphine ligands with five-, resp. eight-atom chains, such as bis(2-diphenylphosphinoethyl) oxide, 1,4-bis(diphenylphosphino)butane (PC<sub>4</sub>P), and 1,5-bis(diphenylphosphino)pentane (PC<sub>5</sub>P) form *tetrahedral* NiX<sub>2</sub> (diphosphine ligand) species with X = Cl, Br, I, whereas Ni(NCS)<sub>2</sub>(**1**) and Ni(NCS)<sub>2</sub>(PC<sub>4</sub>P) are square planar. However, the configuration (*cis*- or *trans*-chelating) of the last two is not known [14–16]. With the longer-chain ligand, 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (POOP), a distorted square planar *trans*-chelate compound, NiI<sub>2</sub>(POOP), was characterized [17]<sup>5</sup>. These flexible-chain diphosphines resemble the prototype ligand system (cyclohexyl)<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>P(cyclohexyl)<sub>2</sub> (n = 3–5) reported by *Issleib* and *Hohlfeld* [18]. Of these, the ligand with n = 5 forms the *trans*-chelate NiCl<sub>2</sub>[(cyclohexyl)<sub>2</sub>-P(CH<sub>2</sub>)<sub>5</sub>P(cyclohexyl)] [18].

In all these examples, 8–11-membered chelate rings are formed. However, the importance of ligand-backbone rigidity is not easily assessed in these cases, since the presence of other than *trans*-chelate species has not been checked except for the ligands **1** and **2**. Comparison between these two ligands clearly shows that the presence of two additional, freely rotating bonds in **1**, relative to **2** is not detrimental to *trans*-chelation.

As stated in the *Introduction*, the appearance of inert metal species other than the *trans*-chelates is likely to reflect kinetic control in complex formation, rather than a thermodynamic preference. The product distribution in complex formation with Pt varied indeed considerably with the reaction conditions. *trans*-[PtCl<sub>2</sub>(**1**)<sub>2</sub>] was formed most efficiently from Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> in benzene, *viz.* under standard conditions for the formation of *trans*-PtX<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> species. Formation of dimer (*ca.* 35%) and a trace of other polymers competed with *trans*-chelate formation (*ca.* 65%) in the analogous reaction with ligand **2**. The most efficient synthesis of *trans*-PtCl<sub>2</sub>(**1**) monomer (87%) was achieved with the use of PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> in a weakly polar solvent mixture (MeCN/toluene 1:100), but PtCl<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> in pure MeCN gave similar yields. The efficient formation of monomer and dimer may be explained in a manner analogous to *Shaw's*

<sup>5</sup>) In contrast to these flexible-chain ether ligands, the O-atom in **1** cannot interact with the metal, if a monomeric complex is formed, since its lone-pair electron density is accumulated at the periphery of the complex.

proposal, concerning the change in entropy of internal rotation [19]. However, in very polar conc. HCl/H<sub>2</sub>O, mostly *cis*-polymers are formed, and this entropy contribution is probably outweighed by strain energy in a transition state of formation of the *cis*-PtCl<sub>2</sub>(**1**) monomer.

In conclusion, the coordination chemistry of **1** is analogous in every respect to that of **2**, despite the greater backbone flexibility. Moderate backbone flexibility is, therefore, not detrimental to the formation of *trans*-spanning chelates, under thermodynamic as well as kinetic control.

The authors thank Dr. P. S. Pregosin, Dr. G. Balimann, and Dr. R. W. Kunz for recording the NMR spectra.

**Experimental.** – Ligand **1** was prepared as described in [8]. Complexes with **1** were prepared in distilled, degassed solvents under pure N<sub>2</sub>. Starting metal compounds were of pure, commercial quality (*Fluka*; *Johnson, Matthey & Co.*) or synthesized according to the literature references given.

**3,3'-Oxybis[ (diphenylphosphinoyl)methylbenzene ].** Ligand **1** (330 mg, 0.58 mmol) was stirred with KMnO<sub>4</sub> (184 mg, 0.58 mmol, analytical reagent) in acetone (85 ml) at r.t. After 3 h, the resulting suspension was filtered. Evaporation of the filtrate gave a residue which was taken up in a few drops of acetone. Addition of a few ml of petroleum ether precipitated a colorless oil which crystallized in the course of a few days. The product was recrystallized from acetone/petroleum ether and dried (24 h, 10<sup>-2</sup> Torr, 20°). <sup>31</sup>P-NMR (CDCl<sub>3</sub>): 29.0. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.7–6.5 (*m*, 28 H); 3.58 (*d*, <sup>2</sup>J(P, H) = 13.5). Anal. calc. for C<sub>38</sub>H<sub>32</sub>O<sub>3</sub>P<sub>2</sub> (598.6): C 76.25, H 5.39, P 10.35; found: C 76.20, H 5.30, P 9.66.

**trans-NiCl<sub>2</sub>(**1**).** A suspension of NiCl<sub>2</sub> · 6 H<sub>2</sub>O (*Fluka*) in acetone (30 ml) was heated to reflux with 2,2-dimethoxypropane (*Fluka, purum*, 2 ml). Ligand **1** (195 mg, 0.82 mmol) was added to the resulting, yellow suspension. Heating to reflux was continued (1 h), until the yellow NiCl<sub>2</sub> precipitate had completely dissolved. Cooling of the mixture (0°) afforded bluish-red crystals which were filtered and dried (430 mg, 75% yield). The crude product was recrystallized (75 ml of CH<sub>2</sub>Cl<sub>2</sub>/acetone 1:2; 332 mg).

**trans-NiBr<sub>2</sub>(**1**).** A suspension of 250 mg (0.75 mmol) of NiBr<sub>2</sub> · 6 H<sub>2</sub>O (obtained by dissolving nickel hydroxide carbonate in HBr and evaporation of the solvent without subsequent dehydration) in acetone (35 ml) was treated with 2,2-dimethoxypropane and heated to reflux (20 min). To the resulting, yellow suspension was added **1** (430 mg, 0.76 mmol), and heating to reflux was continued (3 h). Dark brown crystals separated which were filtered off after cooling (450 mg, 77%). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 3 ml)/acetone (*ca.* 30 ml) afforded 350 mg of pure product.

**trans-NiI<sub>2</sub>(**1**).** A suspension of 315 mg (0.75 mmol) of NiI<sub>2</sub> · 6 H<sub>2</sub>O (obtained in a manner analogous to the bromide, using HI) in acetone (25 ml) was treated with **1** (423 mg, 0.76 mmol). A clear, light-yellow soln. resulted. Acetone (50 ml) and 2,2-dimethoxypropane (5 ml) were added, and the mixture was heated to reflux (1 h). The soln. turned dark, and black crystals were precipitated, which were recovered, dried (235 mg, 36%), and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 10 ml)/acetone (*ca.* 10 ml), yield 200 mg.

**trans-Ni(NCS)<sub>2</sub>(**1**).** To a suspension of Ni(NCS)<sub>2</sub> · 0.5 H<sub>2</sub>O [20] (143 mg, 0.78 mmol) in acetone (35 ml) was added 2,2-dimethoxypropane. After heating to reflux (10 min), **1** was introduced (454 mg, 0.80 mmol). The olive suspension turned orange immediately, and an orange precipitate formed, while the mixture was kept under reflux (3 h). 430 mg (74%) of crude product were filtered off and recrystallized from chlorobenzene (80 ml), to give 325 mg of pure compound.

**trans-Ni(CN)<sub>2</sub>(**1**).** Ni(CN)<sub>2</sub> was precipitated by treating Ni(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub>O with 2 mol of KCN. The resulting gel was collected on a folded paper filter, washed with copious amounts of H<sub>2</sub>O, and dried at 110°. Of this material, 330 mg (≤ 3.0 mmol), along with **1** (1.8 g, 3.2 mmol) and EtOH (10 ml), were placed in a glass vial which was sealed. The reaction was carried out overnight at 100°. After evaporation of the solvent, an orange-yellow oil remained. This was dissolved (CH<sub>2</sub>Cl<sub>2</sub>) and filtered through a membrane filter to remove any undissolved Ni(CN)<sub>2</sub>. The filtrate was stirred with petroleum ether overnight, and crystallization was effected. The crude product (1.38 g, 65%) was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether.

**trans-PdCl<sub>2</sub>(**1**).** (10M, 120 ml) was degassed by heating to reflux under N<sub>2</sub>. The soln. was allowed to cool, and **1** (384 mg, 0.67 mmol) was added. This suspension was heated to 80°, and some of the ligand dissolved. A soln. of PdCl<sub>2</sub> (*Johnson, Matthey & Co., purum*, 120 mg, 0.67 mmol) in HCl (10M, 5 ml) was added at once. A yellow

turbidity developed, and the brown-red color of  $\text{PdCl}_4^{2-}$  disappeared within a few min, with formation of a yellow, flocculent precipitate. The mixture was stirred for 12 h at r.t., and 410 mg (81%) of crude, dry product were obtained. This was solved in  $\text{CH}_2\text{Cl}_2$ , and a small quantity of a white, flocculent residue was filtered off. Addition of toluene to the  $\text{CH}_2\text{Cl}_2$  soln. precipitated another, small amount of white, flocculent impurity, and partial evaporation of the clear filtrate led to crystallization of the pure compound.

*trans-PdBr<sub>2</sub>(1)*.  $\text{PdBr}_2$  (185 mg, 0.71 mmol, prepared by repeated fuming of  $\text{PdCl}_2$  with 48% HBr) was dissolved in MeCN (40 ml) under reflux. Solid **1** (400 mg, 0.70 mmol) was added. Heating to reflux was continued (2 h), and an initial precipitate dissolved to give an orange soln., from which orange crystals deposited. After cooling, acetone (30 ml) was added to complete the crystallization of the complex (510 mg, 87%). The crude product was recrystallized three times from  $\text{CH}_2\text{Cl}_2$ /acetone to afford 340 mg of pure compound.

*trans-PdI<sub>2</sub>(1)*.  $\text{PdI}_2$  was precipitated with NaI from an aq. soln. of  $\text{K}_2\text{PdCl}_4$  (Johnson, Matthey & Co., *purum*). A suspension of  $\text{PdI}_2$  (380 mg, 1.06 mmol) in MeCN was heated to reflux (10 min) and treated with solid **1** (605 mg, 1.07 mmol). An initial, orange-brown precipitate dissolved rapidly, and orange-brown crystals slowly formed. These were filtered off after cooling (685 mg, 70%) and were recrystallized from  $\text{CH}_2\text{Cl}_2$ /acetone (390 mg).

*trans-Pd(N<sub>3</sub>)<sub>2</sub>(1)*. A soln. of  $[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{Pd}(\text{N}_3)_4]$  [21] (520 mg, 0.79 mmol) was heated to reflux (*ca.* 15 min). Upon addition of solid **1** (448 mg, 0.79 mmol), the soln. turned from orange to light yellow, and yellow crystals gradually separated. The mixture was heated for another 3 h, then stirred at r.t. (2 h) and filtered. Yield: 345 mg (57%). The crude product was recrystallized from *ca.* 50 ml  $\text{CH}_2\text{Cl}_2$  by addition of EtOH (40 ml), and 290 mg of pure product were obtained.

*trans-Pd(NO<sub>3</sub>)<sub>2</sub>(1)*. To a soln. of  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (140 mg, 0.53 mmol, *Fluka, purum*) in acetone (100 ml) was added solid **1** (325 mg, 0.57 mmol) and the mixture heated to reflux (30 min). A precipitate formed which is almost completely soluble in the heat. The mixture was evaporated to dryness and dissolved in  $\text{CH}_2\text{Cl}_2$ . An oily fraction remained, and it was separated from soln. by filtration. The clear soln. was evaporated to dryness. Redissolving of the residue in a small quantity of  $\text{CH}_2\text{Cl}_2$  afforded crystals at 0°. These were, however, no more completely soluble in  $\text{CH}_2\text{Cl}_2$ . The suspension containing this insoluble material was filtered, evaporated to dryness, and treated with a small volume of  $\text{CH}_2\text{Cl}_2$ . The resulting crystals (70 mg, 17%) were filtered and dried in the air.

*trans-PtBr<sub>2</sub>(1)*.  $\text{PtBr}_2$  (485 mg, 1.37 mmol) was heated to reflux (1 h) in MeCN (90 ml) to form a yellow suspension. Upon addition of solid **1** (776 mg, 1.37 mmol), a light yellow precipitate formed immediately, which dissolved on further heating (4 h) to give an orange-yellow soln. The mixture was stirred at r.t. overnight, and the resulting yellow solid (900 mg, 71%) was filtered off. The crude product was dissolved in chlorobenzene (*ca.* 80 ml, 50°) and filtered. The filtrate was evaporated to dryness and recrystallized from  $\text{CH}_2\text{Cl}_2$  (*ca.* 50 ml) and MeCN (*ca.* 20 ml). Crystals of pure product (810 mg) formed at 5°.

*trans-PtI<sub>2</sub>(1)*. A mixture of  $\text{PtI}_2$  (530 mg, 1.1 mmol, prepared from  $\text{K}_2\text{PtCl}_4$  and NaI) and of **1** (680 mg, 1.2 mmol) was heated to reflux (12 h) in MeCN (80 ml). An orange precipitate resulted (1.03 g, 85%), which was recrystallized twice from  $\text{C}_6\text{H}_5\text{Cl}$  at 100°, to afford 700 mg of pure product.

*trans-Pt(H)Cl(1)*. Ligand **1** (0.38 g, 0.66 mmol) was added to a degassed benzene (10 ml) soln. of *trans*- $\text{PtHCl}(\text{PPh}_3)_2$  [22] (0.50 g, 0.66 mmol) to form a clear soln. immediately. After stirring (2 h, r.t.) a slight turbidity appeared. Stirring was continued for 12 h, and the solvent was then evaporated under reduced pressure. The white residue was extracted twice with  $\text{Et}_2\text{O}$ , (10 ml) filtered, and washed ( $\text{Et}_2\text{O}$ ). It was then dissolved in benzene (10 ml) and filtered. EtOH (10 ml) was added, and the soln. was evaporated partially in a slow stream of  $\text{N}_2$ . White crystals of *trans*- $\text{Pt}(\text{H})\text{Cl}(\text{1})$  separated. They were filtered, washed and dried *in vacuo* (0.36 g, 68%), m.p. 270° (DSC). IR (CsBr pellet): 2218 (Pt–H).

*trans-Pt(H)Br(1)*. This compound was prepared from *trans*- $\text{Pt}(\text{H})\text{Br}(\text{PPh}_3)_2$  obtained by metathesis from the chloro compound with excess LiBr in acetone [23]. To a degassed benzene soln. (10 ml) of *trans*- $\text{Pt}(\text{H})\text{Br}(\text{PPh}_3)_2$  (0.410 g, 0.499 mmol) was added ligand **1** (0.283 g, 0.499 mmol). The slightly turbid mixture was stirred (12 h, r.t.) and evaporated to dryness under reduced pressure. The residue was worked up as described in the preceding section to yield 0.431 g (71.5%) of hydrido bromo complex, m.p. 263° (DSC). IR: 2216 (Pt–H).

*trans-RhCl(CO)(1)*. Ligand **1** (1.17 g, 1.04 mmol) was dissolved in benzene (100 ml). To the stirred soln. was added at once solid  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$  [24] (400 mg, 1.03 mmol). The resulting yellow, turbid mixture separated a trace of black decomposition products. It was heated to reflux (2 h) and then stirred at r.t. overnight. Of the resulting solid (950 mg, 63%), a sample (400 mg) was treated with MeCN in a Soxhlet extractor. The extraction appeared complete after 12 h, but was continued for another 48 h. The major part of the yellow-white, insoluble material (115 mg) was recovered mechanically from the Soxhlet thimble. The residue from the evaporated MeCN soln. (220 mg) was recrystallized from  $\text{CH}_2\text{Cl}_2$ /MeCN to give pure *trans*-monomer (170 mg, 26%).

*AgCl(1)*. To a soln. of **1** (605 mg, 1.07 mmol) in MeCN (100 ml) was added AgCl (143 mg, 1.0 mmol, freshly recrystallized from  $\text{NH}_3/\text{H}_2\text{O}$  and dried at 0.002 Torr, 20° for 12 h). The mixture was heated to reflux (10 h), then

filtered hot, and evaporated to dryness. The remaining, oily residue was dissolved in acetone, and enough cyclohexane was added to produce a permanent, faint turbidity in the soln. The solvent was evaporated slowly in a stream of  $N_2$  (4–5 bubbles/min). Within two weeks, a few large crystals (edges *ca.* 1–2 mm long) were formed (350 mg, 46%). All further work was done on this crude, solvent-containing product.

**Alternative Syntheses of *trans*-PtCl<sub>2</sub>(1).** *Characterization of Polymeric PtCl<sub>2</sub>(1) Compounds.* *trans*-PtCl<sub>2</sub>(1) was prepared from PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> and 1 as described in [8]. Alternatively, other starting materials, solvents and, reaction conditions were tested (Table 4). Polymeric compounds of the suggested (<sup>1</sup>H-, <sup>31</sup>P-NMR) composition PtCl<sub>2</sub>(1) were obtained in all cases. The amorphous, presumed *cis*-polymers were insoluble in the reaction mixtures and were recovered by filtration. The filtrates contained *trans*-monomer and *trans*-dimer, and these were separated chromatographically [8]. The *trans*-dimer was recovered by elution with benzene/acetone as a slower-moving, yellow band following that of the monomer. Its molecular weight was 1685 (calc. for *trans*-[PtCl<sub>2</sub>(1)]<sub>2</sub>: 1665). The unstable oil resulting after evaporation was characterized by <sup>31</sup>P-NMR and molecular-weight determination. Upon standing in CH<sub>2</sub>Cl<sub>2</sub> soln. at r.t. for several days, > 85% of a *ca.* 1:3 mixture of *trans*-monomer ( $\delta_P$  = 16.31 ppm, <sup>1</sup>J(Pt, P) = 2623 Hz) and *cis*-polymer ( $\delta_P$  = 9.20 ppm, <sup>1</sup>J(Pt, P) = 3712 Hz) was formed.

Depending on the reaction conditions, the white *cis*-polymer fraction was not completely soluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, and thus NMR characterization and molecular-weight determinations were carried out on the soluble fractions. Molecular weights were determined on samples recovered after multiple reprecipitation with polar solvents. Crude samples were dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered (Millipore membrane filters) and precipitated with EtOH or MeCN. After 4 precipitation steps, mol.wt. = 3368 (calc. for *cis*-[PtCl<sub>2</sub>(1)]<sub>4</sub>: 3331) and after 6 reprecipitations, mol.wt. = 4188 (calc. for *cis*-[PtCl<sub>2</sub>(1)]<sub>5</sub>: 4164). It was noted, however, that solns. obtained from residues of evaporation of clear, membrane-filtered solns. were always turbid. These *cis*-polymers are thus somewhat unstable in soln., similarly to the *trans*-dimer.

Evidence for monomeric *cis*-PtCl<sub>2</sub>(1) was always negative (< 2%) in any fresh reaction mixture. However, small amounts of this species ( $\delta_P$  = 9.75 ppm, <sup>1</sup>J(Pt, P) = 3680 Hz) were detected in samples of polymer solns. that had been standing in daylight for several weeks to months, and its mode of formation under these conditions is presently unclear.

**Physical Measurements.** <sup>1</sup>H- and <sup>31</sup>P-NMR spectra were measured at ambient temp. on a Bruker HX 90 instrument in the FT mode at 90, resp. 36.43 MHz. Internal TMS and external H<sub>3</sub>PO<sub>4</sub> standards were used. IR spectra were recorded on a Beckman 4250 instrument to  $\pm 5$  cm<sup>-1</sup> in CsBr pellets or in Nujol suspensions between polyethylene plates. UV/VIS spectra were recorded on a Cary 14 instrument. Molecular-weight determinations and C, H, N, and P elemental analyses were performed by the Organisch-chemisches Mikrolabor, ETH. Metal and halogen determinations were carried out by Prof. B. Magyar and his staff (Laboratorium für Anorganische Chemie, ETH). All of the compounds tenaciously retained nonstoichiometric amounts of solvents which were removed by prolonged (> 72 h) heating (120–180°) *in vacuo*.

**Crystal Structure Determination.** A fragment of one crystal obtained in the preparation (see above) was used. Diffraction data were collected on a Hilger & Watts diffractometer. The structure was solved by the Patterson method. Despite the mediocre crystal quality with its nonstoichiometric occupancy of a solvent site by two different species, an acceptable *R* value was obtained. The population parameters and the temp. factors of C<sub>6</sub>H<sub>12</sub> and (CH<sub>3</sub>)<sub>2</sub>C=O were highly correlated. The solvent populations were, therefore, determined by simultaneously fitting the density, C, H analysis, and molecular-weight data, and kept fixed in subsequent refinements. They were checked independently by comparison with the integrals of the solvent peaks in the <sup>1</sup>H-NMR spectrum (0.58  $\pm$  0.05 mol acetone, 0.29  $\pm$  0.03 mol cyclohexane). The coordinates of C(41) of the acetone molecule were generated by applying a twofold rotation operation on C(40). The H positions were calculated using  $d_{C-H}$  = 0.95 Å. H contributions to the structure factors were included in the refinement ( $U$  = 0.07 Å<sup>2</sup>). Neutral-atom scattering factors for Ag-, Cl-, and P-atoms were taken from [25] with real and imaginary components of anomalous dispersion from [26]. Scattering factors for neutral C- and H-atoms were taken from [25] [27]. Calculations were performed using the X-ray 72 programme system [28] on the CDC 6500 computer of the ETH Zürich. Bond distances, calculated hydrogen positional coordinates and anisotropic displacement parameters of Ag, Cl, P(1), and P(2) may be obtained from the authors.

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