*Organometallics* 1992, *11*, 3879–3885

# Diastereoselective Carbene Insertions into Platinum–Halogen Bonds. Crystal Structure of $[PtCl(\mathit{R}\text{-}CHClCO_2Et)(\mathit{R},\mathit{R}\text{-diop})]$

Paola Bergamini,* Emiliana Costa, and Silvana Sostero

*Dipartimento di Chimica dell'Università di Ferrara e Centro di Fotochimica CNR,*
*Via L. Borsari 46, 44100 Ferrara, Italy*

A. Guy Orpen and Paul G. Pringle*

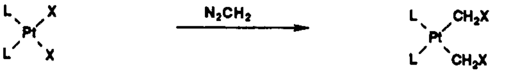
*School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, U.K.*

*Received June 8, 1992*

Ethyl diazoacetate reacts with $[PtX_2L_2]$ [X = Cl, Br, I; $L_2$ = 1,5-cyclooctadiene (cod), 2 $PPh_3$, $Ph_2P(CH_2)_nPPh_2$, *n* = 1 (dppm), 2 (dppe), 3 (dppp), 4 (dppb)] to give the corresponding $[PtX(CHXCO_2Et)L_2]$ as a racemic mixture in high yields. The cod ligands in $[PtX(CHXCO_2Et)(cod)]$ are readily displaced by $PPh_3$ or diphosphines. When optically active complexes $[PtX_2L^*]$ (X = Cl, I; L* = *R*,*R*-diop, *S*,*S*-chiraphos, *S*,*S*-skewphos) were treated with ethyl diazoacetate, the products $[PtX(CHXCO_2Et)L^*]$ were mixtures of diastereoisomers in different proportions. The major diastereoisomer of $[PtCl(CHClCO_2Et)(\mathit{R},\mathit{R}\text{-diop})]$ was readily separated by fractional crystallization, and its crystal structure revealed that the configuration at the $\alpha$-carbon was *R*. This compound is configurationally stable for at least 14 d in $CDCl_3$ solution as shown by $^{31}P$ NMR spectroscopy. Treatment of pure $[PtCl(CHClCO_2Et)(\mathit{R},\mathit{R}\text{-diop})]$ with *S*,*S*-skewphos led to exchange of diphosphines and thereby the assignment of the *S* configuration at the $\alpha$-carbon of the major product of the reaction of $[PtCl_2(\mathit{S},\mathit{S}\text{-skewphos})]$ with ethyl diazoacetate. With the aim of optimizing the diastereoselectivity of the insertion reaction, the chiral diazo ester $N_2CHCO_2R$ (R = *R*,*R*-menthyl) was used as the reagent but it was found that the diastereoselectivities were similar to those with $N_2CHCO_2Et$. The highest diastereoselectivities (up to 7:1) were obtained with $N_2CHCOPh$.

## Introduction

Transition metal complexes are widely used to catalyze carbene-like reactions of diazo carbonyl compounds.[1-6] We[7] and others[8] have reported the reaction of $CH_2N_2$ with $[PtX_2L_2]$ (eq 1) and investigated the chemistry of the products. We were interested in extending this reaction to diazo carbonyl compounds because of the possibility of forming complexes containing an asymmetric PtCHRX moiety. It is shown here that by using chiral diphosphine ligands ready access is obtained to optically stable platinum alkyls containing an asymmetric $\alpha$-carbon atom. A preliminary account of some of these results has been given.[9]



(1)

e.g. $L_2$ = 2$PPh_3$, 1,5-cyclooctadiene, $Ph_2P(CH_2)_nPPh_2$ where n = 1-3 and X = Cl, Br, I

Table I. Elemental Analytical[a] (%) and IR Data[b] ($cm^{-1}$)

| | C | H | $\nu$(C=O) | $\nu$(Pt–Cl) |
|---|---|---|---|---|
| **2a** | 47.54 (47.32) | 4.03 (3.83) | 1720 (s) | 290 (m) |
| **2b** | 42.11 (42.18) | 3.14 (3.39) | 1715 (s, br) | |
| **2c** | 37.59 (37.90) | 3.13 (3.05) | 1720 (s, br) | |
| **2d** | 48.31 (48.04) | 4.00 (4.03) | 1730 (s) | 280 (m) |
| **2e** | 39.10 (38.62) | 3.14 (3.24) | 1730 (s) | |
| **2f**[c] | 47.60 (47.77) | 4.34 (4.14) | 1730 (s, br) | 300 (m) |
| **2g**[c] | 48.30 (48.45) | 4.40 (4.32) | 1730 (s) | 290 (m) |
| **3a** | 31.30 (31.33) | 4.12 (3.94) | 1730 (s) | 320 (m) |
| **3b** | 24.05 (24.41) | 2.69 (2.82) | 1715 (s) | |
| **4a,b** | 54.82 (54.84) | 3.94 (4.14) | 1740 (s) | 295 (m) |
| **7a, 8a** | 47.91 (48.00) | 4.31 (4.41) | 1730 (s) | 300 (m) |
| **7b, 8b**[d] | 46.88 (46.67) | 4.44 (4.11) | 1730 (s) | 285 (m) |
| **7c, 8c** | 48.91 (49.40) | 4.38 (4.40) | 1725 (s, br) | 300 (m) |
| **10a, 11a** | 40.99 (40.66) | 3.73 (3.68) | 1720 (s) | |
| **10b, 11b** | 41.25 (40.65) | 3.79 (3.72) | 1710 (s) | |
| **14a, 15a**[d] | 50.02 (49.67) | 3.99 (4.13) | 1680 (s) | 300 (m) |
| **14b, 15b**[e] | 51.33 (51.95) | 4.16 (4.27) | 1680 (s) | 300 (m) |
| **16a, 17a**[e] | 43.00 (42.80) | 3.48 (3.52) | 1670 (s) | |
| **16b, 17b**[e] | 42.48 (42.88) | 3.45 (3.53) | 1670 (s) | |

[a] Calculated values in parentheses. [b] Spectra measured in CsI pellets; s = strong, br = broad, m = medium. [c] Contains 0.25 $CH_2Cl_2$ as shown by $^1H$ NMR. [d] Contains 1 $CH_2Cl_2$ as shown by $^1H$ NMR. [e] Contains 0.5 $CH_2Cl_2$ as shown by $^1H$ NMR.

## Results and Discussion

Jennings et al[10] have reported that complexes such as *cis*- and *trans*-$[PtCl(CHClCO_2Et)(py)_2]$ can be made by

---

(1) (a) Doyle, M. P.; van Oeveren, A.; Westrum, L. J.; Protopopova, M. N.; Clayton, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 8982. (b) Hashimoto, S.-I.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1990**, *31*, 5173.

(2) (a) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K.-L. *J. Am. Chem. Soc.* **1990**, *112*, 1906. (b) Nakamura, A.; Koyama, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 593. (c) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443. (d) Becalski, A.; Cullen, W. R.; Fryzuk, M. D.; Herb, G.; James, B. R.; Kutney, J. P.; Piotrowska, K.; Tapiolas, D. *Can. J. Chem.* **1988**, *66*, 3108. (e) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645.

(3) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094.

(4) (a) Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssie, P.; *J. Chem. Soc., Chem. Commun.* **1981**, 688. (b) Demonceau, A.; Noels, A. F.; Costa, J.-L.; Hubert, A. J. *J. Mol. Catal.* **1990**, *58*, 21.

(5) Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssié, P. *J. Org. Chem.* **1981**, *46*, 873.

(6) (a) Armstrong, K. R. *J. Org. Chem.* **1966**, *31*, 618. (b) Werner, H.; Richards, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 4976.

(7) Alcock, N. W.; Pringle, P. G.; Bergamini, P.; Sostero, S.; Traverso, O. *J. Chem. Soc., Dalton Trans.* **1990**, 1553.

(8) (a) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; Rice, R. E.; McLees, A. C. *J. Chem. Soc., Dalton Trans.* **1988**, 1773. (b) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McLees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (c) McCrindle, R.; Ferguson, G.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1524. (d) McCrindle, R.; Ferguson, G.; Arsenault, G. J.; Hampden-Smith, M. J.; McAlees, A. J.; Ruhl, B. L. *J. Organomet. Chem.* **1990**, *390*, 121. (e) McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J.; Ruhl, B. L.; Sneddon, D. W. *Organometallics* **1986**, *5*, 1171. (f) McCrindle, R.; Arsenault, G. J.; Farwaha, R. *J. Organomet. Chem.* **1985**, *236*, C51. (g) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466. (h) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464.

(9) Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A. G.; Pringle, P. G.; *Organometallics* **1991**, *10*, 2989.

(10) Hanks, T. W.; Ekeland, R. A.; Emerson, K.; Larsen, R. D.; Jennings, P. W. *Organometallics* **1987**, *6*, 28.

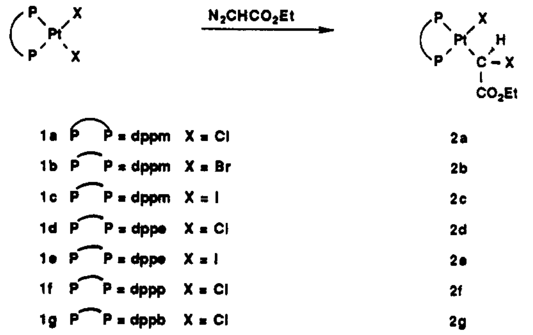
0276-7333/92/2311-3879$03.00/0

Table II. $^{31}$P NMR Data[a]

| | $\delta(P_A)$ | $^1J(PtP_A)$ | $\delta(P_B)$ | $^1J(PtP_B)$ | $^2J(P_AP_B)$ | ratio[b] |
|---|---|---|---|---|---|---|
| **2a** | −47.7 | 3485 | −49.9 | 1645 | 56 | |
| **2b** | −50.1 | 3702 | −53.6 | 1663 | 56 | |
| **2c** | −56.3 | 3620 | −58.6 | 1700 | 56 | |
| **2d** | 40.8 | 4011 | 39.9 | 2092 | 5 | |
| **2e** | 41.8 | 3875 | 40.3 | 2041 | 5 | |
| **2f** | −1.3 | 3901 | −5.3 | 1929 | 30 | |
| **2g** | 20.6 | 4143 | 1.8 | 1948 | 20 | |
| **4a** | 23.9 | 3098 | | | | |
| **4b** | 19.4 | 4301 | 18.3 | 1982 | 20 | |
| **5a,b** | 41.4 | 3972 | 39.9 | 2102 | 5 | 1.0 |
| | 40.9 | 3984 | 39.4 | 2097 | 5 | |
| **7a**[c] | 1.5 | 4099 | −0.5 | 1946 | 20 | 3.0[d] |
| **8a**[c] | 1.5 | 4099 | −1.3 | 1932 | 20 | |
| **7b** | 10.9 | 3960 | 8.7 | 1980 | 27 | 2.0[d] |
| **8b**[e] | 11.5 | 3921 | 7.3 | 1902 | 27 | |
| **7c, 8c** | 41.3 | 3872 | 40.0 | 2063 | 15 | 3.0[d] |
| | 41.3 | 3972 | 40.0 | 1997 | 15 | |
| **10a, 11a** | −5.3 | 3894 | −8.8 | 2033 | 17 | 3.0[d] |
| | −4.6 | 3869 | −11.3 | 2026 | 17 | |
| **10b, 11b** | 4.8 | 3716 | 3.8 | 2053 | 24 | 1.0[d] |
| | 6.0 | 3762 | 0.7 | 1997 | 27 | |
| **10c, 11c** | 38.5 | 3762 | 37.4 | 2051 | 15 | 1.5[d] |
| | 40.1 | 3608 | 37.8 | 2241 | 15 | |
| **12a, 13a** | 1.2 | 4076 | −0.9 | 1928 | 20 | 2.5 |
| | −0.9 | 4082 | −2.0 | 1922 | 20 | |
| **12b, 13b** | 11.4 | 3943 | 7.1 | 1924 | 27 | 1.0 |
| | 11.0 | 3913 | 7.1 | 1924 | 27 | |
| **14a, 15a** | 0.7 | 4072 | −0.6 | 1995 | 20 | 5.0 |
| | −0.2 | 4072 | −1.9 | 2000 | 20 | |
| **14b, 15b** | 10.4 | 3885 | 8.0 | 2011 | 27 | 7.0[f] |
| | 8.9 | 3909 | 9.1 | 1994 | 27 | |
| **16a, 17a** | −6.9 | 3884 | −8.6 | 2103 | 17 | 5.0 |
| | −6.2 | 3860 | −12.3 | 2063 | 19 | |
| **16b, 17b** | 3.3 | 3771 | 2.6 | 2092 | 27 | 1.0 |
| | 1.8 | 3715 | 0.1 | 2048 | 27 | |

[a] Spectra (36.2 MHz) measured in $CDCl_3$ at 28 °C unless otherwise stated. Chemical shifts ($\delta$) in ppm (±0.1) to high frequency of 85% $H_3PO_4$. Coupling constants ($J$) in Hz (±3). $P_A$ is trans to the halogen and $P_B$ is trans to the carbon. [b] In cases where two diastereoisomers are formed numbers in this column refer to ratios of the intensities of the $^{31}$P NMR signals (data for the major isomer are given first unless stated otherwise). [c] Some of the signals were coincident in $CDCl_3$ but in $(CD_3)_2SO$ they are all clearly resolved: **7a**, $\delta(P_A)$ 2.4, $^1J(PtP_A)$ = 4057, $\delta(P_B)$ −0.5, $^1J(PtP_B)$ = 1970, $^2J(P_AP_B)$ = 20; **8a**, $\delta(P_A)$ 2.9, $^1J(PtP_A)$ = 4050, $\delta(P_B)$ −1.4, $^1J(PtP_B)$ = 1965, $^2J(P_AP_B)$ = 20. [d] A 1:1 mixture of the isomers has been generated from **3a** or **3b** to verify that these intensities are valid measures of the diastereomeric excess (see text). [e] Major isomer. [f] Relative intensities the same when the spectrum was measured with gated decoupling (no NOE) and with a pulse delay of 5 s.

treatment of Zeise's dimer with $N_2CHCO_2Et$ followed by addition of pyridine. We now report that upon addition of an excess of $N_2CHCO_2Et$ to complexes of the type [$PtX_2$(diphosphine)] (**1a–g**) in $CH_2Cl_2$, $N_2$ is evolved and [PtX($CHXCO_2Et$)(diphosphine)] (**2a–g**), the products of monoinsertion, are obtained (eq 2). The complexes **2a–g** have been characterized by a combination of elemental analysis and IR and $^{31}$P and $^1$H NMR spectroscopy (see Tables I–III).



(2)

Table III. $^1$H NMR Data[a]

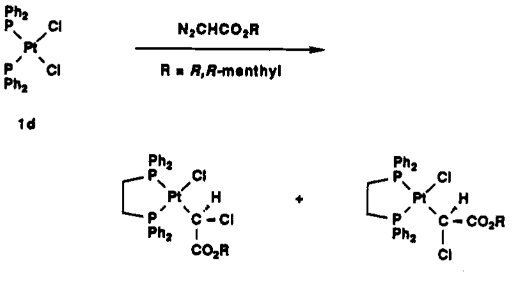
| | $\delta(PtCH)$ | $^2J(PtCH)$ | $^3J(PPtCH)$ | other[b] |
|---|---|---|---|---|
| **2a** | 4.75 | 97 | 9.3 | $\delta(CH_2P)$ 4.20, 4.35 |
| **2b** | 4.78 | 91 | 7.0 | $\delta(CH_2P)$ 4.20, 4.42 |
| **2c** | 4.72 | 87 | 6.6 | $\delta(CH_2P)$ 4.22, 4.42 |
| **2d** | 4.41 | 70 | 10.5, 6.9 | $\delta(CH_2P)$ 2.10, 2.40 (m) |
| **2e** | 4.66 | 78 | 9.3 | $\delta(CH_2P)$ 2.20 (m) |
| **2g** | 3.71 | 53 | 10.5 | |
| **3a** | 4.92 | 109 | | $\delta$(cod) 2.30, 2.60 (m), 4.93, 5.15, 5.75 |
| **3b** | 5.24 | 100 | | $\delta$(cod) 2.20, 2.50 (m), 4.70, 5.62, 5.80 |
| **4b** | 3.98 | 59 | 11.2, 8.4 | |
| **7a** | 4.10 | | | $\delta(CH_3)$ 1.03, 1.21 |
| **8a** | 4.10 | | | $\delta(CH_3)$ 0.98, 1.24 |
| **7b, 8b** | 3.83 | 58 | 9.6 | $\delta(CH_3)$ 1.10, 1.25 |
| **7c, 8c** | 4.30 | 80 | 9.3, 6.5 | $\delta(CH_3)$ 1.08 (m) |
| | 4.36 | nr | 8.8, 6.0 | |
| **10a, 11a** | 3.65 (m)[c] | nr | nr | $\delta(CH_3)$ 0.83, 1.05, 1.08, 1.15 |
| **10b, 11b** | 3.80 (m)[c] | nr | nr | $\delta(CH_3)$ 1.0 (m) |
| **14a, 15a** | 4.55 | 74 | 10.9 | $\delta(CH_3)$ 1.05, 1.25 |
| **14b, 15b** | 4.81 | 79 | 9.0 | $\delta(CH_3)$ 1.05 (m) |
| **16a, 17a** | 4.50 (m)[c] | nr | nr | $\delta(CH_3)$ 0.80, 1.20, 1.15, 1.28 |
| **16b, 17b** | 4.75 (m) | nr | nr | $\delta(CH_3)$ 1.0 (m), 1.20 (m) |

[a] Spectra (300 MHz) measured in $CDCl_3$ at 25 °C; chemical shifts ($\delta$) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants ($J$) in Hz (±0.1). nr = not resolved. [b] Signals for $CH_3$ groups on the diop, skewphos, or chiraphos ligands unless otherwise stated; m = multiplet. [c] Assignment confirmed by COSY.

Similarly, treatment of [$PtX_2$(cod)] (X = Cl, I) with $N_2CHCO_2Et$ in $CH_2Cl_2$ gave the corresponding [PtX($CHXCO_2Et$)(cod)] (**3a**, X = Cl; **3b**, X = I). Complexes **3a,b** provide an alternative route to [PtX($CHXCO_2Et$)(diphosphine)] by displacement of cod (Scheme I). Substitution of cod with $PPh_3$ gave the trans isomer of [PtX($CHXCO_2Et$)($PPh_3$)$_2$] (**4a**) almost exclusively whereas when *cis*-[$PtCl_2(PPh_3)_2$] is treated with with $N_2CHCO_2Et$ in $CDCl_3$ the cis isomer **4b** is the major product. Neither **4a** nor **4b** isomerized in $CDCl_3$ over a period of 3 h, but upon addition of $PPh_3$ to these solutions, some isomerization did occur very slowly (see Scheme I).

The presence of the asymmetric $\alpha$-carbons in **2a–c** is readily apparent from their $^1$H NMR spectra, which show the inequivalence of the diastereotopic backbone $CH_2$ protons (see Table III for the data). Clearly all the complexes **2a–g** are racemic mixtures, but it was reasoned that, by using optically active diazo reagents or optically active ancillary ligands, diastereoisomers would be obtained which may be separable.

Hence [$PtCl_2$(dppe)] (**1d**) was treated with $N_2CHCO_2R$ (R = *R,R*-menthyl) in $CDCl_3$, and the products were analyzed in solution by $^{31}$P NMR. Two AB patterns were observed, as expected for the formation of the diastereomers **5a** and **5b** (eq 3), but unfortunately the intensities of the signals for the two isomers were the same, indicating that this reaction was not diastereoselective.

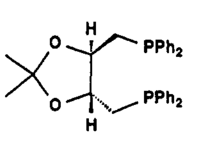


**1d**

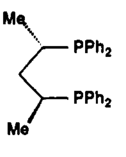
**5a** **5b**

(3)

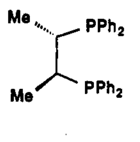
More success in terms of diastereoselectivity was achieved by treatment of the platinum complexes **6a–c** of the optically active ligands *R,R*-diop, *S,S*-skewphos, and *S,S*-chiraphos with $N_2CHCO_2Et$. Figure 1 shows the $^{31}P$ NMR spectrum of the products obtained from the reaction of $[PtCl_2(S,S\text{-skewphos})]$ (**6b**) with $N_2CHCO_2Et$ in $CDCl_3$. The spectrum, which is typical, contains two similar AB patterns consistent with the formation of the diastereoisomers **7b** and **8b** (eq 4). The intensities of the $^{31}P$ NMR signals for **7b** and **8b** are in the ratio ca. 1:2, respectively (see below for the assignment of the absolute configuration). The validity of using $^{31}P$ NMR intensities to estimate the diastereomeric excess in this case was demonstrated by the following experiment: *S,S*-skewphos was added to racemic $[PtCl(CHClCO_2Et)(cod)]$ (**3a**) to give the products **7b** and **8b** as a 1:1 mixture, and the $^{31}P$ NMR spectrum showed the same AB patterns as above but in almost exactly 1:1 intensity ratio (see Figure 1).



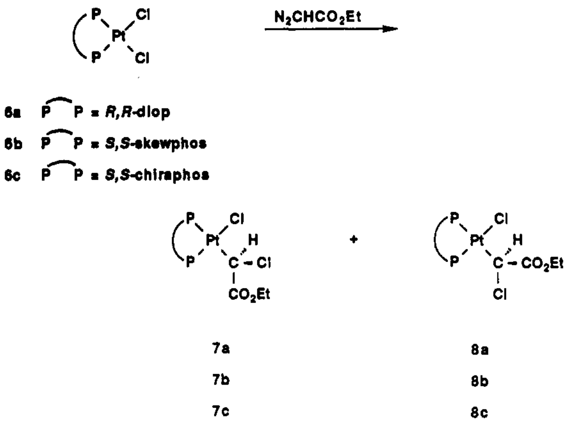
*R,R*-diop



*S,S*-skewphos



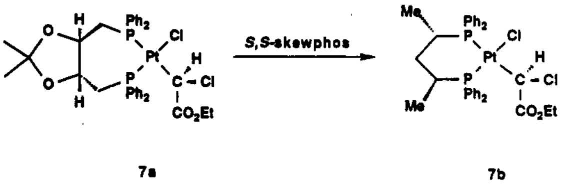
*S,S*-chiraphos



(4)

In a similar fashion, the reactions of **6a** and **6c** with $N_2CHCO_2Et$ gave mixtures of **7a**, **8a** and **7c**, **8c** in the ratios shown in Table II; both of these mixtures have been isolated and fully characterized (see Tables I–III for characterizing data).

The absolute configuration at the α-carbon in the major isomer of $[PtCl(CHClCO_2Et)(R,R\text{-diop})]$ is *R* (i.e. complex **7a**) as shown by X-ray crystallography (see below). No isomerization of **7a** to **8a** in $CDCl_3$ was detected by $^{31}P$ NMR over a period of 14 days. The absolute configuration at the α-carbon for the major product of the reaction of $N_2CHCO_2Et$ with **6b** was assigned *S* on the basis of the reaction of the pure diastereomer **7a** with *S,S*-skewphos, which generated the minor isomer **7b** (eq 5).



(5)

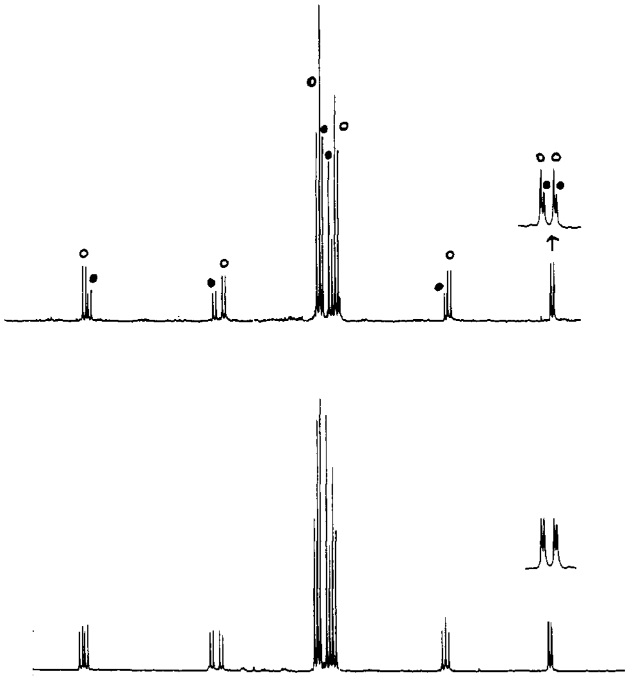


**Figure 1.** $^{31}P$ NMR spectrum (36.4 MHz) of the mixture of the two diastereoisomers of $[PtCl(CHClCO_2Et)(S,S\text{-skewphos})]$, **7b** (●) and **8b** (○), formed upon (a) treatment of $[PtCl_2(S,S\text{-skewphos})]$ with $N_2CHCO_2Et$ and (b) treatment of $[PtCl(CHClCO_2Et)(cod)]$ with *S,S*-skewphos.

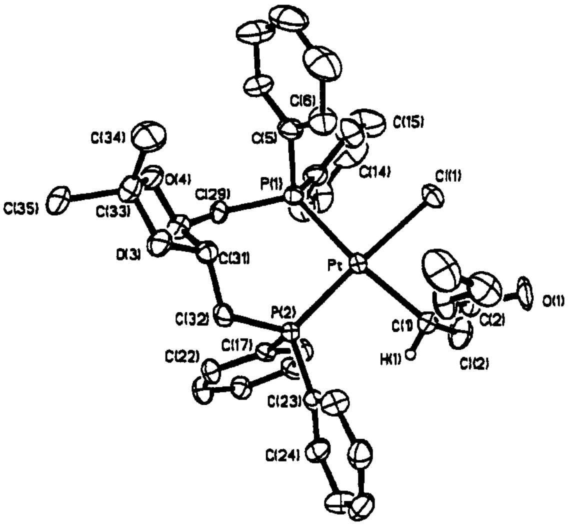


**Figure 2.** Molecular geometry of **7a**, showing the atom-labeling scheme. Non-hydrogen atoms are represented as ellipsoids enclosing 30% probability density. All hydrogens other than H(1) have been omitted for clarity.

The molecular structure of **7a**, as present in crystals of its dichloromethane solvate, is shown in Figures 2 and 3, and the molecular dimensions are listed in Table IV. The crystal structure consists of isolated molecules of **7a** and $CH_2Cl_2$ separated by normal contacts (there is a weak C–H⋯O contact between solvent and one of the *R,R*-diop oxygens, C(36)⋯O(4) = 3.49 Å). The molecule **7a** consists of a platinum atom chelated by an *R,R*-diop ligand and further ligated by a chloride ligand and σ-bonded to the chiral alkyl ligand through C(1) [Pt–C(1) = 2.114 (13) Å]. The variation in trans influence is indicated by the different Pt–P distances for the two *R,R*-diop phosphorus atoms [Pt–P(1) = 2.320 (3) Å trans to C(1), and Pt–P(2) = 2.233 (3) Å trans to Cl(1); Pt–Cl(1) = 2.362 (3) Å]. As is to be expected for a platinum(II) complex, the coordination at Pt is essentially planar (mean deviation of 0.065 Å) with a slight twist (6.5°) in the coordination plane between the $PtP_2$ and the PtCCl units. The cis and trans angles deviate slightly from 90 and 180°, the largest deviation for a cis angle being for the *R,R*-diop ligand [P(2)–Pt(2)–P(1) = 96.3 (1)°]. The conformation adopted by the chiral alkyl has the α-hydrogen near the coordination plane of the platinum and pointing toward phenyl

**Scheme I. Synthesis and Reactions of [PtCl(CHClCO$_2$Et)(cod)] (3a)**

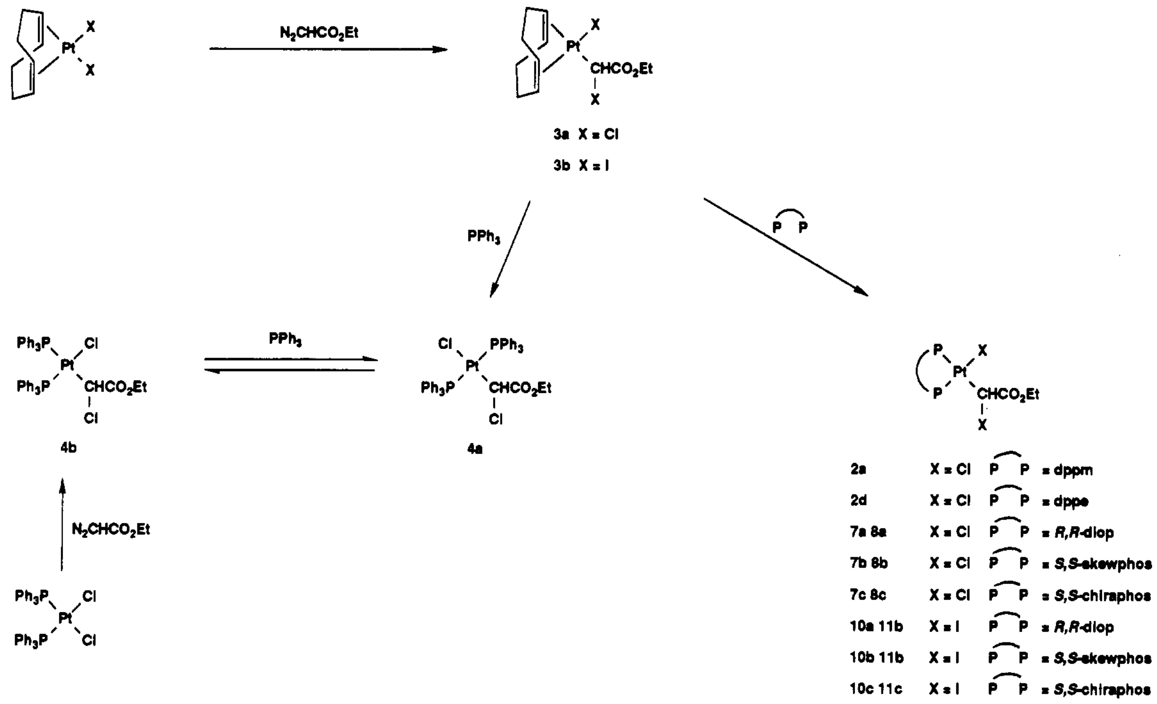


**Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for 7a•CH$_2$Cl$_2$**

| | | | | | |
|---|---|---|---|---|---|
| Pt–P(1) | 2.320 (3) | Pt–P(2) | 2.233 (3) | Pt–Cl(1) | 2.362 (3) |
| Pt–C(1) | 2.114 (13) | P(1)–C(5) | 1.830 (13) | P(1)–C(11) | 1.821 (13) |
| P(1)–C(29) | 1.820 (15) | P(2)–C(17) | 1.817 (11) | P(2)–C(23) | 1.812 (13) |
| P(2)–C(32) | 1.851 (12) | Cl(2)–C(1) | 1.803 (14) | O(1)–C(2) | 1.214 (15) |
| O(2)–C(2) | 1.346 (18) | O(2)–C(3) | 1.424 (21) | C(1)–H(1) | 0.84 (13) |
| C(1)–C(2) | 1.450 (18) | C(3)–C(4) | 1.444 (30) | O(3)–C(31) | 1.446 (20) |
| O(3)–C(33) | 1.420 (18) | O(4)–C(30) | 1.429 (14) | O(4)–C(33) | 1.418 (20) |
| C(5)–C(6) | 1.365 (21) | C(5)–C(10) | 1.348 (21) | C(6)–C(7) | 1.421 (29) |
| C(7)–C(8) | 1.418 (35) | C(8)–C(9) | 1.280 (40) | C(9)–C(10) | 1.387 (25) |
| C(11)–C(12) | 1.404 (22) | C(11)–C(16) | 1.353 (22) | C(12)–C(13) | 1.350 (27) |
| C(13)–C(14) | 1.397 (35) | C(15)–C(14) | 1.308 (33) | C(15)–C(16) | 1.399 (26) |
| C(17)–C(18) | 1.387 (17) | C(17)–C(22) | 1.396 (15) | C(18)–C(19) | 1.361 (19) |
| C(19)–C(20) | 1.404 (19) | C(20)–C(21) | 1.358 (19) | C(21)–C(22) | 1.399 (19) |
| C(23)–C(24) | 1.412 (18) | C(23)–C(28) | 1.415 (18) | C(24)–C(25) | 1.415 (22) |
| C(25)–C(26) | 1.331 (23) | C(26)–C(27) | 1.416 (22) | C(27)–C(28) | 1.364 (20) |
| C(29)–C(30) | 1.529 (25) | C(30)–C(31) | 1.519 (26) | C(31)–C(32) | 1.484 (21) |
| C(33)–C(34) | 1.492 (24) | C(33)–C(35) | 1.544 (22) | C(36)–Cl(3) | 1.691 (30) |
| C(36)–Cl(4) | 1.685 (28) | | | | |

| | | | |
|---|---|---|---|
| P(1)–Pt–P(2) | 96.3 (1) | P(1)–Pt–Cl(1) | 86.7 (1) |
| P(2)–Pt–Cl(1) | 176.9 91) | P(1)–Pt–C(1) | 170.3 (4) |
| P(2)–Pt–C(1) | 91.0 (3) | Cl(1)–Pt–C(1) | 86.1 (3) |
| Pt–P(1)–C(5) | 116.1 (5) | Pt–P(1)–C(11) | 108.8 (4) |
| C(5)–P(1)–C(11) | 105.2 (7) | Pt–P(1)–C(29) | 120.2 (5) |
| C(5)–P(1)–C(29) | 104.5 (7) | C(11)–P(1)–C(29) | 100.0 (7) |
| Pt–P(2)–C(17) | 110.7 (4) | Pt–P(2)–C(23) | 116.9 (4) |
| C(17)–P(2)–C(23) | 103.4 (5) | Pt–P(2)–C(32) | 115.8 (4) |
| C(17)–P(2)–C(32) | 109.2 (5) | C(23)–P(2)–C(32) | 99.8 (6) |
| C(2)–O(2)–C(3) | 119.2 (11) | Pt–C(1)–Cl(2) | 107.9 (6) |
| Pt–C(1)–H(1) | 104 (10) | Cl(2)–C(1)–H(1) | 98 (10) |
| Pt–C(1)–C(2) | 112.7 (9) | Cl(2)–C(1)–C(2) | 112.3 (9) |
| H(1)–C(1)–C(2) | 121 (10) | O(1)–C(2)–O(2) | 120.4 (13) |
| O(1)–C(2)–C(1) | 129.6 (14) | O(2)–C(2)–C(1) | 110.0 (10) |
| O(2)–C(3)–C(4) | 107.3 (15) | C(31)–O(3)–C(33) | 105.8 (11) |
| C(30)–O(4)–C(33) | 109.1 (12) | P(1)–C(29)–C(30) | 116.7 (11) |
| O(4)–C(30)–C(29) | 111.6 (13) | O(4)–C(30)–C(31) | 99.1 (13) |
| C(29)–C(30)–C(31) | 117.5 (11) | O(3)–C(31)–C(30) | 102.5 (13) |
| O(3)–C(31)–C(32) | 108.9 (12) | C(30)–C(31)–C(32) | 117.3 (13) |
| P(2)–C(32)–C(31) | 116.0 (9) | O(3)–C(33)–O(4) | 106.6 (11) |
| O(3)–C(33)–C(34) | 112.0 (14) | O(4)–C(33)–C(34) | 108.5 (14) |
| O(3)–C(33)–C(35) | 106.6 (12) | O(4)–C(33)–C(35) | 110.2 (13) |
| C(34)–C(33)–C(35) | 112.7 (14) | Cl(3)–C(36)–Cl(4) | 114.4 (17) |

ring C(23–28) on P(2) [torsion angle P(2)–Pt–C(1)–H(1) = 5 (10)°]. This orientation allows the bulkier Cl and CO$_2$Et substituents at C(1) to avoid the crowded Pt coordination plane.

The reactions shown in eq 4 offer a very simple entry into alkylplatinum(II) complexes containing an asymmetric

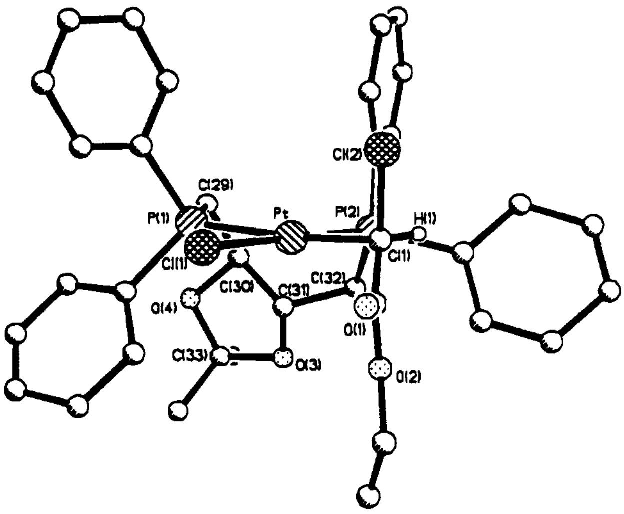
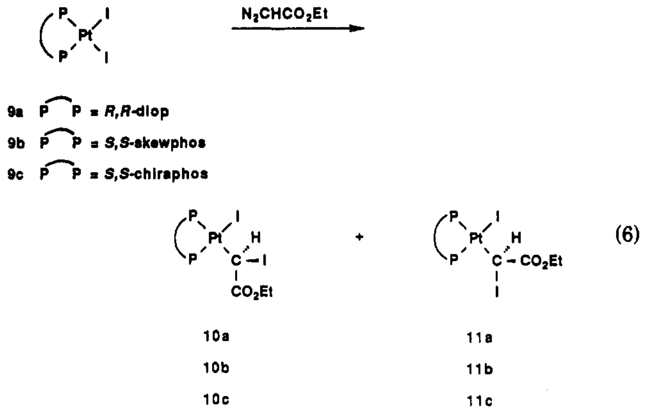
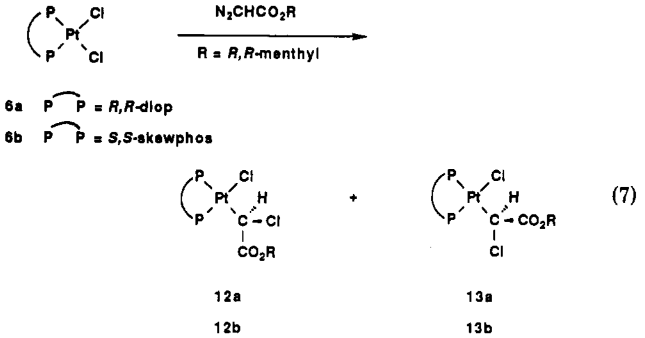


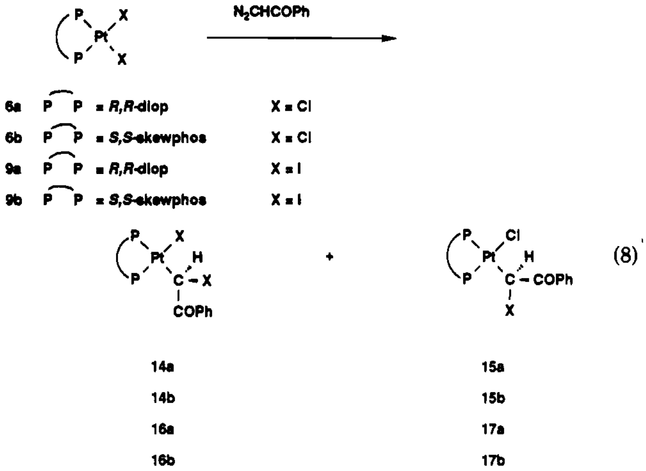
**Figure 3.** Alternative view of the structure of **7a**. All hydrogen atoms except H(1) have been omitted for clarity.



(6)



(7)



(8)

$\alpha$-carbon atom.[11] Alkylmetal complexes of this type can provide valuable stereochemical information on the course of fundamental organometallic reactions[12] such as metal–carbon insertions or reductive eliminations, and they are pivotal intermediates in the mechanisms of many metal-catalyzed asymmetric syntheses.[13] Thus the intrinsic interest in these products prompted us to investigate the generality of this insertion reaction by varying the halide ligand (eq 6) and the diazo carbonyl compound (eqs 7 and 8). All of these reactions were followed by $^{31}P$ NMR spectroscopy, and the results are presented in Table II; some of the products have been isolated and completely characterized (see Tables I–III).

The diiodo complexes **9a–c** react with $N_2CHCO_2Et$ to give the products of monoinsertion, **10a–c** and **11a–c**, with the diastereoselectivities shown in Table II. Once again the validity of using $^{31}P$ intensities to estimate the diastereoselectivity was checked by comparison with a spectrum of a 1:1 mixture of **10a–c** and **11a–c** made from [PtI(CHICO$_2$Et)(cod)] and the appropriate diphosphine ligand. It was concluded that the diastereoselectivity of Pt–X insertion is not greatly dependent on the halogen (Cl, I).

It was hoped that the combination of chiral diazoester and chiral complexes would lead to higher diastereoselectivity for the $\alpha$-carbon configuration. Hence the dichloro complexes **6a** and **6b** were treated with $N_2CHCO_2R$ (R = *R,R*-menthyl) and the ratios of the products **12a**:**13a** and **12b**:**13b** estimated from the $^{31}P$ NMR spectra (see Table II), but disappointingly a diastereomeric excess similar to that observed with $N_2CHCO_2Et$ was obtained.

The best diastereoselectivities (up to 7:1) were obtained with $N_2CHCOPh$. Treatment of **6a**, **6b**, **9a**, or **9b** with $N_2CHCOPh$ (eq 8) gave the corresponding products **14a,b** with **15a,b** and **16a,b** with **17a,b** (see Tables I–III for characterizing data).

At present the factors determining the diastereoselectivity of the insertions reported here are not predictable. This is amply illustrated by comparing the results for the reaction of $N_2CHCOPh$ with the dichloro complexes **6a** and **6b** and the diiodo complexes **9a** and **9b** (eq 8). The diastereomeric ratios for both of the dichloro complexes are high and indicate that, in this case, the *S,S*-skewphos ligand engenders higher selectivity than *R,R*-diop. However for the diiodo complexes, while the *R,R*-diop complex gives a high diastereomeric ratio (similar to the dichloro analogue), the *S,S*-skewphos complex gives essentially no diastereoselectivity at all.

The relative rates of reactions between $N_2CHCOR$ (R = OEt, Ph) and [PtX$_2$(*R,R*-diop)] (X = Cl, I) were followed by $^{31}P$ NMR (see Experimental Section for conditions), and from these measurements we are able to draw the following qualitative conclusions: (a) the diiodo complex reacts faster than the dichloro complex; (b) the diazo ester reacts faster than the diazo ketone; (c) the rates of reaction are similar in DMSO and $CDCl_3$.

The reaction temperature and solvent ($CDCl_3$, $CD_3CN$, $(CD_3)_2SO$) have no apparent effect on the diastereoselectivity. For example, no difference was observed in the diastereoselectivity when the addition of $N_2CHCO_2Et$ to **6a** was carried out at −40 °C (when the reaction was much slower) or +65 °C in $CHCl_3$, which suggests that diaster-

---

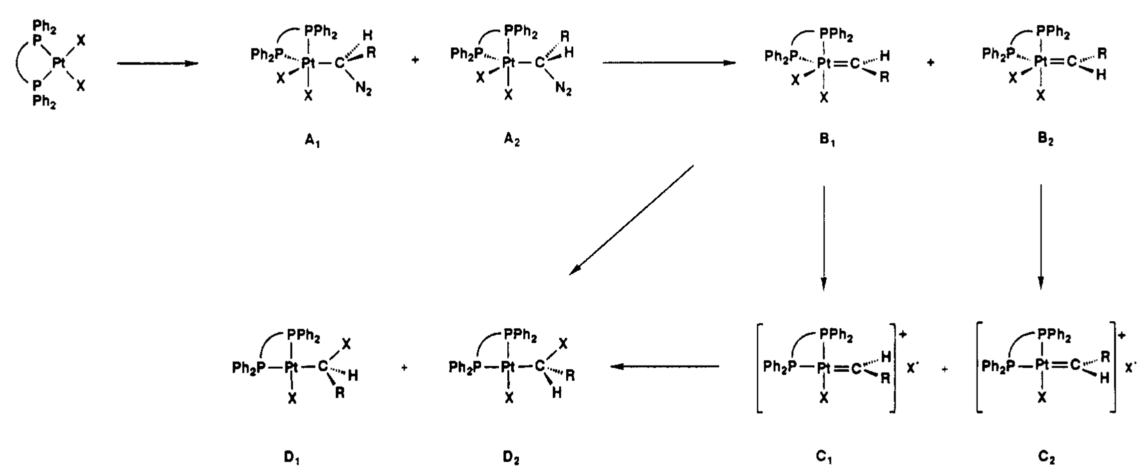
[11] (a) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 625. (b) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838.

[12] Flood, T. C. *Topics in Inorganic and Organometallic Stereochemistry*; J. Wiley and Sons: New York, 1981.

[13] (a) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon; Oxford, V. K., 1982; Vol. 8, p 463. (b) Reference 1 in: Chu, K.-H.; Foxman, B. M.; Rosenblum, M.; Zhu, X.-Y. *Organometallics* **1990**, *9*, 3010.

[14] Reference deleted in revision.

**Scheme II. Proposed Mechanism for the Insertions of $N_2CHCOR$ (R = EtO, Ph) into Pt–X (X = Cl, I) Bonds (P$\frown$P = diop, skewphos, or chiraphos)**



eoselectivity is not kinetically controlled.

Scheme II is a suggested mechanism based on that previously proposed[7,8a] for the insertion of $CH_2N_2$ into Pt–Cl bonds. Without a detailed quantitative kinetic analysis of the reactions, we are unable to say whether the origin of the diastereoselectivity is kinetic (i.e. differential energies of formation or rates of reaction of the diastereomeric intermediates A–C) or thermodynamic (i.e. simply a result of the relative stabilities of the products $D_1$ and $D_2$).

## Conclusion

The reaction of diazo carbonyl compounds with complexes of the type $[PtX_2(diphosphine)]$ giving products containing the asymmetric moiety PtCHX(COR) has been shown to be a general one. When the ancillary ligands are optically active, diastereoselectivity was observed, and it has been demonstrated that it is possible to separate the diastereoisomers readily and to determine the absolute configuration. The use of these compounds in mechanistic and synthetic chemistry is under investigation.

## Experimental Section

All reactions were carried out under an atmosphere of nitrogen, though the products could be handled in air. $CH_2Cl_2$ was distilled from $CaH_2$ under nitrogen. All the diphosphines (Aldrich) and $N_2CHCOOEt$ (Fluka) were used as purchased and $N_2CHCOO$–*R,R*-menthyl[15] and $N_2CHCOPh$[16] were made by literature methods. Infrared spectra (CsI disks) were obtained using a Perkin-Elmer 283B spectrophotometer. $^{31}P\{^1H\}$ NMR spectra were measured either at 36.4 MHz and 28 °C using a Jeol FX90 spectrometer or at 162 MHz and 25 °C using a Jeol FX400 spectrometer; $^1H$ NMR spectra were measured at 300 MHz and 25 °C using a Varian Gemini 300 spectrometer.

**Preparation of [PtCl(CHClCO$_2$Et)(dppm)] (2a) from [PtCl$_2$(dppm)] (1a).** A 400-μL volume (3.80 mmol) of $N_2CHCOOEt$ was added to a solution of 300 mg (0.46 mmol) of $[PtCl_2(dppm)]$ in 20 mL of $CH_2Cl_2$ and the mixture stirred for 48 h. The solvent was then removed under vacuum and the residue recrystallized from $CH_2Cl_2/Et_2O$ to give 250 mg (74%) of the white solid product. Complexes **2b–g** and **4b** were made similarly in 60–80% yields.

**Preparation of [PtCl(CHClCO$_2$Et)(cod)] (3a).** $[PtCl_2(cod)]$ (0.50 g, 1.34 mmol) was dissolved in $CH_2Cl_2$ (50 mL) and 150 μL (1.4 mmol) of $N_2CHCOOEt$ added dropwise under nitrogen. The resulting yellow solution was stirred for 48 h at room temperature, and then the solvent was removed under vacuum to give an oily, yellow solid which was recrystallized from $CH_2Cl_2/n$-pentane to give pure **3a** as a microcrystalline solid (0.497 g, 1.08 mmol, 80% yield). Complex **3b** was made similarly in 89% yield.

**Preparation of [PtCl(*R*-CHClCO$_2$Et)(*R,R*-diop)] (7a) from [PtCl$_2$(*R,R*-diop)] (6a).** A 200-μL volume (1.87 mmol) of $N_2CHCOOEt$ in 2 mL of $CHCl_3$ was added to a solution of 200 mg (0.26 mmol) of [PtCl$_2$(*R,R*-diop)] in 10 mL of $CHCl_3$ and the mixture stirred for 2 h. Then the mixture was reduced to dryness under vacuum and the resulting oil redissolved in 5 mL of $CH_2Cl_2$ followed by 50 mL of *n*-pentane to precipitate 188 mg (85%) of product which is a mixture of stereoisomers **7a** and **8a**. Recrystallization from $CH_2Cl_2/Et_2O$ yielded 70 mg of pure **7a**.

[PtCl(CHClCO$_2$Et)(*S,S*-skewphos)] (**7b**, **8b**) and [PtCl(CHClCO$_2$Et)(*S,S*-chiraphos)] (**7c**, **8c**) were made similarly from 5 equiv of $N_2CHCOOEt$ and **6b** and **6c** in 65 and 60% yield, respectively; in these cases no attempt was made to separate the isomers. Also [PtI(CHICO$_2$Et)(*S,S*-skewphos)] (**10b**,**11b**) was made this way from **9b** and 2 equiv of $N_2CHCOOEt$ in 79% yield.

**Preparation of [PtI(CHICO$_2$Et)(*R,R*-diop)] (10a, 11a) from [PtI(CHICO$_2$Et)(cod)] (3b).** A 178-mg amount (0.357 mmol) of *R,R*-diop in 30 mL of $CH_2Cl_2$ was added dropwise to a solution of 230 mg (0.357 mmol) of [PtI(CHICO$_2$Et)(cod)] (**3b**) in 20 mL of $CH_2Cl_2$ and the mixture stirred for 1 h. The solvent was then removed under vacuum to give a yellow solid, which was triturated with $Et_2O$ to give 252 mg (68%) of product.

The following were made in a similar manner from [PtX(CHXCO$_2$Et)(cod)] (**3a**, **3b**): **2a** (74%), **2d** (79%), **4a** (82%), and 1:1 mixtures of **7a** and **8a**, **7b** and **8b**, **7c** and **8c**, **10a** and **11a**, **10b** and **11b**, and **10c** and **11c** were generated in $CDCl_3$ solution from **3a** or **3b** and the appropriate diphosphine and characterized by $^{31}P$ NMR only.

**Preparation of [PtCl(CHClCOPh)(*S,S*-skewphos)] (14b, 15b) from [PtCl$_2$(*S,S*-skewphos)] (6b).** A 150-mg amount (0.21 mmol) of **6b** was dissolved in 3 mL of $CH_2Cl_2$, and 124 mg (0.85 mmol) of $PhCOCHN_2$ was added and the mixture stirred for 48 h. The solvent was then removed under vacuum and 1 mL of $CH_2Cl_2$ readded followed by 10 mL of $Et_2O$ added to precipitate 135 mg (77%) of the pale yellow product.

Complexes **14a**, **15a** and **14c**, **15c** were made similarly. Because of the low reactivity of $PhCOCHN_2$, high concentrations and long reaction times are necessary for syntheses involving this compound.

**NMR Reactions.** Some of the products (**5a**, **10c**, **12a**, **12b** with their corresponding diastereoisomers) reported here were characterized only in solution by $^{31}P$ NMR spectroscopy. In these cases the precursor dihaloplatinum complex (0.03 mmol) was dissolved in 0.3 mL of $CDCl_3$ and the diazo compound (3–5 equivalents) added. $N_2$ was evolved, and once this had subsided, the spectrum was recorded.

Relative rates were estimated by $^{31}P$ NMR spectroscopy as follows. A 26.16 mM stock solution was prepared from 500 mg (0.654 mmol) of [PtCl$_2$(*R,R*-diop)] in 25 mL of $CDCl_3$. A 0.75-mL volume of this solution (0.019 6 mmol of complex) was then treated with 14.3 mg (0.098 mmol, 5.0 equiv) of $PhCOCHN_2$ and the course of the reaction followed by measuring the $^{31}P$ NMR spectra every 20 min. The progress of the reactions between [PtCl$_2$-

---

[15] Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553.

[16] Scott, L. T.; Minton, M. A. *J. Org. Chem.* **1977**, *42*, 3757.

**Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for 7a•$CH_2Cl_2$**

| atom | *x* | *y* | *z* | $U_{eq}{}^a$ |
|---|---|---|---|---|
| Pt | 1799 (1) | 0 | 8662 (1) | 33 (1) |
| P(1) | 3018 (3) | 747 (2) | 7396 (2) | 38 (1) |
| P(2) | 3619 (3) | −518 (2) | 9558 (2) | 32 (1) |
| Cl(1) | −200 93) | 496 (3) | 7764 (3) | 60 (1) |
| Cl(2) | −170 (4) | 358 (3) | 10610 (3) | 74 (1) |
| O(1) | −1848 (8) | −895 (8) | 9353 (10) | 70 (4) |
| O(2) | −92 (9) | −1677 (6) | 8851 (10) | 66 (4) |
| C(1) | 472 (12) | −500 (8) | 9822 (11) | 44 (4) |
| H(1) | 1004 (137) | −703 (88) | 10293 (115) | 50 |
| C(2) | −618 (12) | −1001 (10) | 9341 (11) | 54 (4) |
| C(3) | −995 (19) | −2298 (11) | 8419 (16) | 82 (6) |
| C(4) | −216 (22) | −2813 (14) | 7697 (20) | 105 (9) |
| O(3) | 5754 (10) | −1417 (6) | 7001 (7) | 55 (3) |
| O(4) | 5963 (10) | −129 (7) | 6235 (7) | 57 (4) |
| C(5) | 2680 (15) | 474 (10) | 5978 (10) | 55 (4) |
| C(6) | 1828 (16) | −174 (9) | 5706 (13) | 65 (6) |
| C(7) | 1531 (25) | −337 (16) | 4597 (20) | 105 (9) |
| C(8) | 2112 (26) | 195 (20) | 3813 (15) | 103 (12) |
| C(9) | 3006 (27) | 741 (21) | 4105 (16) | 116 (11) |
| C(10) | 3265 (18) | 920 (12) | 5188 (11) | 71 (6) |
| C(11) | 2576 (14) | 1852 (8) | 7502 (11) | 52 (4) |
| C(12) | 3179 (17) | 2347 (10) | 8321 (15) | 73 (6) |
| C(13) | 2819 (23) | 3156 (14) | 8456 (22) | 102 (9) |
| C(14) | 1809 (29) | 3495 (13) | 7769 (20) | 103 (10) |
| C(15) | 1185 (27) | 3036 (13) | 7035 (20) | 110 (10) |
| C(16) | 1569 (18) | 2201 (10) | 6884 (16) | 77 (6) |
| C(17) | 4492 (11) | 301 (7) | 10325 (8) | 36 (3) |
| C(18) | 3707 (12) | 938 (9) | 10755 (11) | 46 (4) |
| C(19) | 4226 (15) | 1529 (9) | 11442 (11) | 52 (4) |
| C(20) | 5633 (13) | 1518 (8) | 11698 (11) | 49 (4) |
| C(21) | 6409 (13) | 899 (10) | 11275 (12) | 58 (5) |
| C(22) | 5898 (11) | 297 (7) | 10550 (10) | 46 (4) |
| C(23) | 3297 (12) | −1313 (9) | 10565 (9) | 41 (4) |
| C(24) | 3505 (15) | −1191 (10) | 11686 (11) | 53 (4) |
| C(25) | 3139 (18) | −1835 (11) | 12409 (12) | 69 (6) |
| C(26) | 2579 (15) | −2551 (10) | 12070 (13) | 63 (5) |
| C(27) | 2315 (14) | −2681 (9) | 10953 (13) | 59 (5) |
| C(28) | 2693 (14) | −2080 (7) | 10236 (11) | 50 (4) |
| C(29) | 4874 (15) | 816 (11) | 7514 (14) | 43 (5) |
| C(30) | 5674 (10) | 4 (14) | 7349 (8) | 46 (3) |
| C(31) | 4946 (18) | −815 (10) | 7582 (15) | 43 (5) |
| C(32) | 4876 (11) | −1080 (7) | 8728 (9) | 40 (3) |
| C(33) | 6202 (15) | −995 (11) | 6063 (12) | 62 (5) |
| C(34) | 5420 (21) | −1260 (15) | 5072 (15) | 93 (8) |
| C(35) | 7752 (16) | −1165 (13) | 5990 (14) | 77 (6) |
| C(36) | 8362 (33) | 1128 (16) | 4964 (22) | 145 (13) |
| Cl(3) | 7752 (18) | 2119 (7) | 4939 (8) | 259 (9) |
| Cl(4) | 8044 (11) | 578 (5) | 3823 (5) | 149 (4) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(*R*,*R*-diop)] and $EtO_2CCHN_2$, [$PtI_2$(*R*,*R*-diop)] and $EtO_2CCHN_2$, and [$PtCl_2$(*R*,*R*-diop)] and $EtO_2CCHN_2$ in DMSO was followed similarly.

**Structure Analysis of [Pt(*R*,*R*-diop){*R*-$CHClCO_2Et$}Cl] (7a·$CH_2Cl_2$).** Crystal data for 7a·$CH_2Cl_2$: $C_{36}H_{39}Cl_4P_2Pt$, $M_r$ = 870.6, monoclinic, space group $P2_1$ (No. 4), $a$ = 9.775 (2) Å $b$ = 15.964 (2) Å, $c$ = 12.376 (3) Å, $\beta$ = 91.31 (2)°, $U$ = 1930.8 (7) Å$^3$, $Z$ = 2, $D_x$ = 1.50 g cm$^{-3}$, $\lambda$ = 0.710 69 Å, $\mu$(Mo K$\alpha$) = 40.7 cm$^{-1}$, $F$(000) = 926, $T$ = 293 K.

## X-ray Experimental Section

A single crystal of 7a·$CH_2Cl_2$ (approximate dimensions 0.30 × 0.45 × 0.60 mm) was mounted in a thin-walled glass capillary under $N_2$ and held in place with epoxy glue. All diffraction measurements were made at room temperature (293 K) on a Nicolet P3m diffractometer, using graphite-monochromated Mo K$\alpha$ X-radiation. Unit cell dimensions were determined from 25 centered reflections in the range $16.0 < 2\theta < 29.0°$. A total of 3882 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by Wyckoff $\omega$ scans. Three check reflections (236, 523, $11\bar{1}$) remeasured after every 100 ordinary data showed no decay and variation of ±3% over the period of data collection. Of the 3755 intensity data (other than checks) collected, 3546 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 3277 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied in the basis of 525 azimuthal scan data; maximum and minimum transmission coefficients were 0.235 and 0.095, respectively. Lorentz and polarization corrections were applied.

The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms, fixed isotropic displacement parameters. All non-hydrogen atoms and hydrogen atom H(1) (which was located in a difference Fourier synthesis) were refined without positional constraints. All other hydrogen atoms were constrained to idealized geometries (C–H = 0.96 Å, H–C–H = 109.5°). A parameter ($\eta$) defining the absolute structure and hence the molecular chirality[17] refined to 1.00 (5), thereby confirming the handedness of the molecules of 7a in the crystal studied. Full-matrix least-squares refinement of this model (427 parameters) converged to final residual indices $R$ = 0.038, $R_w$ = 0.047, and $S$ = 1.35 [$R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum w\Delta^2/\sum wF_o{}^2]^{1/2}$; $S = [\sum w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$]. Weights, $w$, were set equal to $[\sigma_c{}^2(F_o) + gF_o{}^2]^{-1}$, where $\sigma_c{}^2(F_o)$ is the variance in $F_o$ due to counting statistics and $g$ = 0.0008 was chosen to minimize the variation in $S$ as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +1.4 to −1.6 e Å$^{-3}$, the largest of these being close to the platinum atom. Table V lists the final atomic positional parameters for the freely refined atoms, and Table IV, the selected derived bond lengths and interbond angles. Tables S1–S5, which have been deposited as supplementary material, provide the final atomic positional parameters for the non-hydrogen atoms and full lists of the derived bond lengths and interbond angles, the anisotropic displacement parameters, and the hydrogen atomic parameters, respectively. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[18] Complex neutral-atom scattering factors were taken from ref 19.

**Acknowledgment.** We should like to thank Prof. O. Traverso (Università di Ferrara) for useful discussions, Ciba-Geigy for the Senior Research Fellowship (to P.G.P.), NATO for the provision of a travel grant, and Johnson-Matthey for a generous loan of platinum salts.

**Supplementary Material Available:** Full listings of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates for 7a·$CH_2Cl_2$ (4 pages). Ordering information is given on any current masthead page.

OM920325R

---

(17) Rogers, D. *Acta Crystallogr., Sect. A* **1981**, *37*, 734.

(18) Sheldrick, G. M. SHELXTL-PLUS Rev. 2.4. Göttingen, FRG, 1988.

(19) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.