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Reactions of Diazo Carbonyls with [PtX(CH$_3$)(chiral diphosphine)] (X = Cl, Br, I): Chemoselectivity and Diastereoselectivity of Pt−C and Pt−X Carbene Insertion

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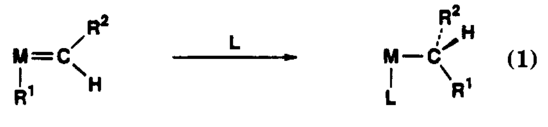
In polar solvents (e.g. MeCN), ethyl diazoacetate reacts with [PtXMe(*S*,*S*-diop)], where *X* = Cl, Br, I, to give the corresponding [PtX(CHMeCO$_2$Et)(*S*,*S*-diop)] as a 2:1 mixture of diastereoisomers in high yields. The major diastereoisomer of [PtCl(CHMeCO$_2$Et)(*S*,*S*-diop)] is readily separated in crystalline form, and its crystal structure reveals that the configuration at the α-carbon is *R*; it is configurationally stable in CDCl$_3$ for at least 14 days. The factors that influence the diastereoselectivity have been examined by comparing (by ^{31}P NMR spectroscopy) the ratio of diastereoisomers formed in the reactions between [PtXMe(diphos*)] and N$_2$CHCOR: X = Cl, Br, I; diphos* = *S*,*S*-diop, *R*,*R*-diop, *S*,*S*-skewphos, *S*,*S*-chiraphos; R = OEt, O(*l*-menthyl), Ph. In MeCN, the diastereoselectivity is independent of halogen but is a sensitive function of the chiral diphosphine and diazo carbonyl, though no systematic correlations have been divined. In solvents of lower polarity (e.g. CH$_2$Cl$_2$), diazo carbonyls react with [PtXMe(diphos*)] to give the products derived from Pt−X insertion as well as Pt−C insertion. When C$_6$H$_6$ is used as the solvent, the compounds [PtMe(CHICOR)(*S*,*S*-diop)], where R = OEt, O(*l*-menthyl), Ph, are formed in high yields and have been isolated. Redissolving these compounds in MeCN did not lead to isomerization to the Pt−C insertion species [PtI(CHMeCOR)(*S*,*S*-diop)]. Several trends have been found relating the extent of Pt−C insertion to the nature of the solvent and the structure of the reagents: the proportion of Pt−C insertion increases with (i) increasing polarity of the solvent (C$_6$H$_6$ < CHCl$_3$ < CH$_2$Cl$_2$ < (CH$_3$)$_2$SO), (ii) increasing nucleofugacity of the halogen (I < Br < Cl), (iii) decreasing bite angle of the diphosphine (diop < chiraphos, skewphos), and (iv) diazo ketone < diazo ester. A mechanism which is consistent with these observations is discussed. Many of the compounds discussed here have been observed in solution only by ^{31}P NMR, but representative species have been isolated and fully characterized by a combination of elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectroscopy.

Introduction

One of the most important processes in organometallic chemistry, particularly in relation to organic synthesis and homogeneous catalysis, is the formation of a C−C bond within the coordination sphere of a transition metal.[1] The migration of an alkyl group to a coordinated carbene (eq 1) is an important C−C bond forming step in the Fischer−Tropsch synthesis,[2] and recently this reaction (eq 1) has been exploited in organic and organometallic syntheses.[3] We were interested in the insertion of substituted carbenes (RCH) into the Pt−C bonds of chiral methylplatinum(II) complexes because of the possibility of controlling the configuration at the stereogenic center created α to the metal. In this paper we report that the reaction between diazo carbonyls and substrates of the type [PtX(CH$_3$)(chiral diphosphine)] (eq 2) can result in both Pt−C and Pt−X insertion occurring and in most cases these reactions are diastereoselective. A preliminary account of some of this work has been given.[4]



(1)

Results and Discussion

When [PtX(CH$_3$)(*S*,*S*-diop)] (X = Cl (**1a**), Br (**1b**), I (**1c**)) is treated with 1 equiv of N$_2$CHCO$_2$Et in CD$_3$CN or (CD$_3$)$_2$SO, nitrogen is evolved and, in each case, two products in the ratio 2:1 are observed by ^{31}P NMR spectroscopy (see Table 1 for the data) whose structures have been assigned as **2a−c** and **3a−c** (Scheme 1) on

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1995.

[1] For leading references see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

[3] For leading references see: (a) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 464. (b) Trace, R. L.; Sanchez, J.; Young, J.; Yim, S.; Jones, W. M. *Organometallics* **1992**, *11*, 1440. (c) Adams, H.; Bailey, N. A.; Bentley, G. W.; Tattershall, C. E.; Taylor, B. F.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 533.

[4] Bergamini, P.; Costa, E.; Cramer, P.; Hogg, J.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1994**, *14*, 1058.

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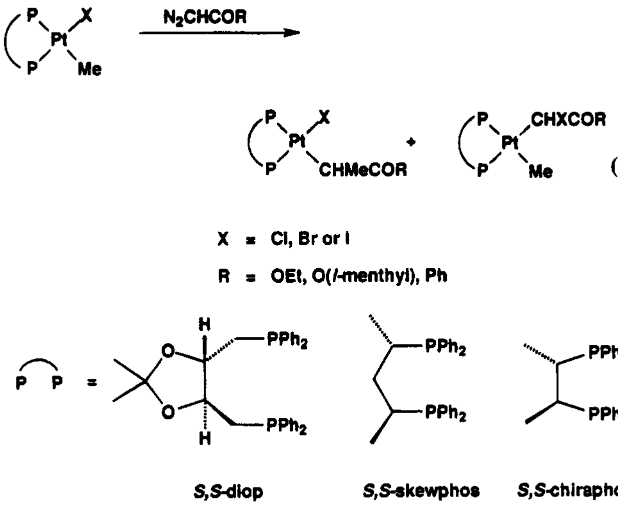


(2)

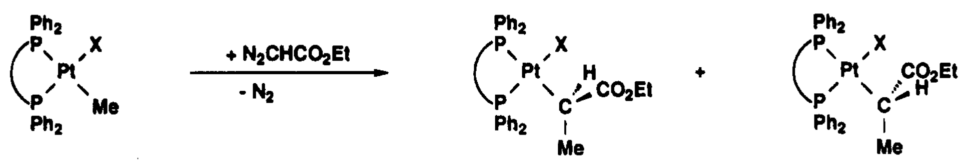
the following evidence. The major product from the reaction of **1a** was crystallized and its structure determined to be **2a** by X-ray crystallography (see below). The minor product is assigned the diastereoisomeric structure **3a** on the basis of the similarity of the spectroscopic data for **2a** and **3a** (Table 1 and Experimental Section). Reaction of the appropriate halide salt with pure **2a** gave the pure bromo and iodo analogues (**2b** and **2c**), and with 2:1 mixtures of **2a** and **3a**, 2:1 mixtures of **2b** and **3b** and of **2c** and **3c** were formed. Though it has previously been suggested[5] that complexes containing a chiral $CHMeCO_2Et$ ligand would be susceptible to racemization via a β-hydrogen elimination mechanism, no epimerization was observed when solutions of pure chloro complex **2a** or bromo complex **2b** in $CDCl_3$ were left to stand for 14 days. The iodo complexes **2c** and **3c** are more labile: after a few hours in $CDCl_3$, significant decomposition had taken place and one of the byproducts was identified as the diiodo complex $[PtI_2$(*S,S*-diop)].

X-ray Crystal Structure of 2a. The molecular structure of **2a**, as present in the solid state, is shown in Figure 1, and the molecular dimensions are listed in Table 2. The crystal structure consists of isolated molecules of **2a** separated by normal contacts. The molecule **2a** consists of a platinum atom which is chelated by a diop ligand and further ligated by a chloride ligand and σ-bonded to the chiral alkyl ligand through C(8) (Pt–C(8) = 2.171(14) Å). The variation in *trans* influence is indicated by the different Pt–P distances for the two diop phosphorus atoms (Pt–P(1) = 2.227(4) *trans* to Cl(1) and Pt–P(2) = 2.331(4) *trans* to C(8)). As is to be expected for a platinum(II) complex, the coordination at Pt is slightly distorted from planar (mean deviation of 0.112 Å) with a slight twist (10.8°) 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 diop ligand (P(2)–Pt(1)–P(1) = 100.1(1)°). The conformation adopted by the chiral alkyl has the α-hydrogen near the coordination plane of the platinum and pointing toward P(1) (torsion angle P(1)–Pt–C(8)–H(8a) = 16.5°). This orientation allows the bulkier Me and CO_2Et substituents at C(8) to avoid the crowded Pt coordination plane. Rather similar gross geometry was observed in [PtCl(*R*-$CHClCO_2Et$)(*R,R*-diop)], albeit with the opposite absolute structure.[6] It should be noted that the favored diastereomeric configuration at the chiral α-carbon is the same in [PtCl(*R*-$CHClCO_2Et$)(*R,R*-diop)] and [PtCl(*R*-$CHMeCO_2Et$)(*S,S*-diop)] (**2a**).

Diastereoselectivity. In order to map the factors that influence the diastereoselectivity of the Pt–C insertions, we have systematically varied the ancillary diphosphine ligand, the halogen ligand, the solvent, and the diazo reagent as described below.

The complexes [PtX(CH_3)(*S,S*-skewphos)] (**4a–c**) and [PtX(CH_3)(*S,S*-chiraphos)] (**5a–c**) were treated with 1 equiv of N_2CHCO_2Et and the ratios of the diastereoisomeric products (Scheme 1) determined by the integration of the ^{31}P NMR signals (Table 1). The chloro complexes **6a**, **7a** and **8a**, **9a** were isolated, but the bromo and iodo analogues were characterized only in solution by ^{31}P NMR spectroscopy. The configuration of the α-carbon in the major isomer **6a** was determined to be *R* by observing that treatment of pure **2a** with *S,S*-skewphos in CH_2Cl_2 (eq 3) gave only **6a**. In DMSO, the skewphos substrates **4a–c** gave greater (5:1) diastereoselectivity than the diop substrates (2:1), while the chiraphos substrates **5a–c** gave negligible (1:1) diaste-

Scheme 1



1a	X = Cl	$\widehat{P\ P}$ = *S,S*-diop	**2a**	**3a**
1b	X = Br	$\widehat{P\ P}$ = *S,S*-diop	**2b**	**3b**
1c	X = I	$\widehat{P\ P}$ = *S,S*-diop	**2c**	**3c**
4a	X = Cl	$\widehat{P\ P}$ = *S,S*-skewphos	**6a**	**7a**
4b	X = Br	$\widehat{P\ P}$ = *S,S*-skewphos	**6b**	**7b**
4c	X = I	$\widehat{P\ P}$ = *S,S*-skewphos	**6c**	**7c**
5a	X = Cl	$\widehat{P\ P}$ = *S,S*-chiraphos	**8a**	**9a**
5b	X = Br	$\widehat{P\ P}$ = *S,S*-chiraphos	**8b**	**9b**
5c	X = I	$\widehat{P\ P}$ = *S,S*-chiraphos	**8c**	**9c**

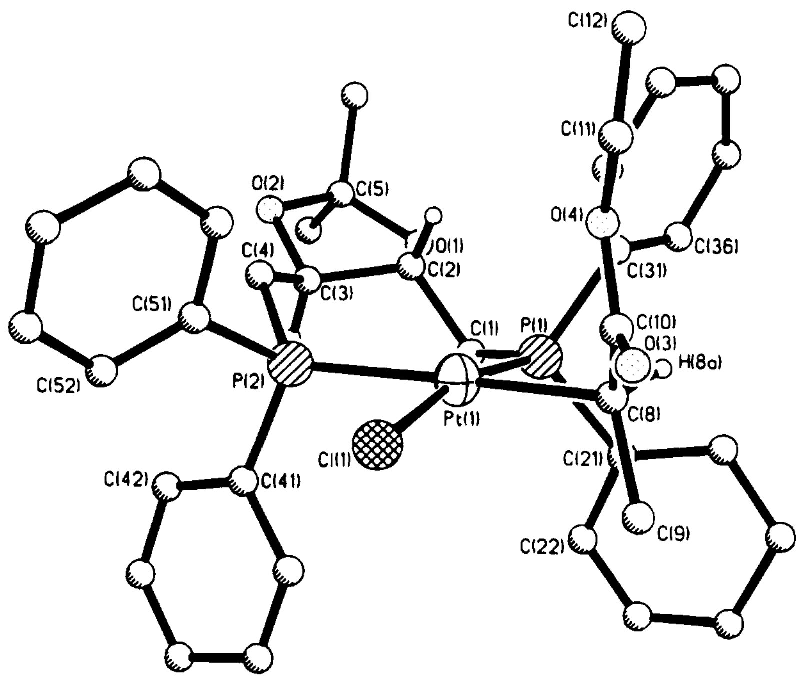
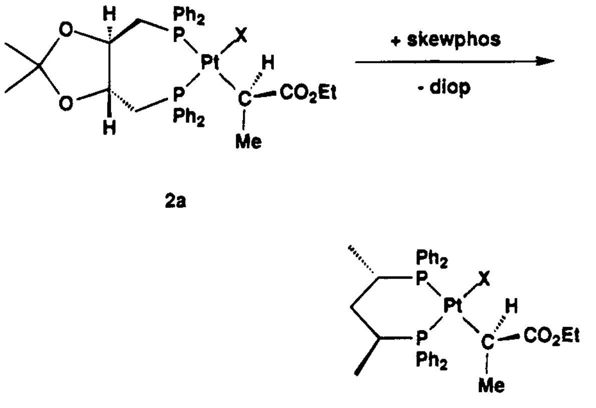


Figure 1. Molecular geometry of **2a**, showing the atom-labeling scheme. Non-hydrogen atoms are represented as ellipsoids enclosing 30% probability density. All hydrogens other than H(2a), H(3a), and H(8a) have been omitted for clarity.



2a

(3)

6a

reoselectivity. Hence, as expected, the diastereoselectivity of the Pt–C insertion is a function of the chiral ligand.

It was noted in the reactions shown in Scheme 1 that in polar solvents (MeCN, DMSO), the ratio of diastereoisomers was independent of the halogen. However, in less polar solvents ($CHCl_3$, CH_2Cl_2, C_6H_6) the ratios differ from those in polar solvents and depend on the halogen. For example, in DMSO and MeCN, the ratio of the skewphos products **6a–c**:**7a–c** is 5:1 for each of the halogens while in $CDCl_3$ the ratios are as follows: **6a**:**7a**, 2.5:1; **6b**:**7b**, 1.5:1; **6c**:**7c**, 1:1. This rather complex dependence of the diastereoselectivity on solvent and halogen will be discussed later.

To probe the effect of changing the diazo carbonyl reagent, [PtX(CH_3)(*S*,*S*-diop)] (**1a–c**) or the enantiomers [PtX(CH_3)(*R*,*R*-diop)] (**1a′–c′**) were treated with diazoacetophenone or *l*-menthyl diazoacetate to give **10–15** (Scheme 2). The complexes **12a**, **13a** and **14a**, **15a** have been isolated, but the other products of the reactions shown in Scheme 2 were identified only by ^{31}P NMR spectroscopy, and none of the absolute configurations have been determined. The ratio of diastereoisomers is sensitive to the structure of the diazo carbonyl: the ratio of the products derived from diazoacetophenones **10a–c** and **11a–c** was essentially 1:1 while for the menthyl ester complexes **12a–c** and **13a–c** the ratio was 4:1 (*cf.* 2:1 for the products from N_2CHCO_2Et). The subtlety of this sensitivity is illustrated by the reaction of [PtX(CH_3)(*R*,*R*-diop)] (**1a′–c′**) with *l*-menthyl diazoacetate, which in MeCN gives the products **14a–c**:**15a–c** in the ratio of 2:1. This discrimination between the enantiomers by *l*-menthyl diazoacetate indicates that some double diastereoselectivity is operating in this reaction; i.e. *l*-menthyl diazoacetate and **1a** are matched reagents.[7] Interestingly, when a 1:1 mixture of the enantiomers **1a** and **1a′** is treated with 1 equiv of *l*-menthyl diazoacetate at 20 °C, reaction takes place preferentially with **1a**: the ratio of the products derived from **1a** and **1a′** is 2:1 (see Experimental Section).

The reaction of N_2CHCO_2Et with the bromo complex **1b** in $CDCl_3$ was carried out at +60, +20, and −15 °C and the diastereomeric ratio of the Pt-C insertion products found to be 2:1, 3:1, and 4:1 respectively; i.e., this reaction is more diastereoselective at lower temperatures.

Chemoselectivity. It was shown by ^{31}P NMR spectroscopy that addition of N_2CHCO_2Et to [PtI(CH_3)(*S*,*S*-diop)] (**1c**) in CH_2Cl_2 gave not only the expected mixture of **2c** and **3c** but also the new species **16c** and **17c**, the products of carbene insertion into the Pt–I bond (Scheme 3). It was found that the relative proportions of the two sets of products (**2c**, **3c** and **16c**, **17c**) was a function of the solvent in which the reaction was carried out (see below). Thus, treatment of **1c** with N_2CHCO_2Et in DMSO or MeCN gave **2c** and **3c** exclusively, while in benzene **16c** and **17c** constitute *ca.* 85% of the product.

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[5] Flood, T. C. In *Topics in Inorganic and Organometallic Stereochemistry*; Wiley: New York, 1981; p 37.

[6] Bergamini, P.; Costa, E.; Sostero, S.; Orpen, A. G.; Pringle, P. G. *Organometallics* **1992**, *11*, 3879.

[7] Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

Table 1. ^{31}P and ^{195}Pt NMR Data[a]

	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^1J(PtP_B)$	$^2J(P_AP_B)$	ratio[b]	$\delta(Pt)$
1a	7.33	4318	10.10	1675	13		
1b	8.18	4295	7.70	1710	13		
1c	7.04	4104	3.49	1762	14		
2a	5.56	4305	5.07	1807	15	2.0 (2.0)	
3a	2.77	4296	3.30	1769	17		
2b	4.93	4294	2.74	1832	16	3.5 (2.0)	
3b	1.74	4282	0.23	1802	17		
2c	0.70	4113	−1.96	1868	16	3.0 (2.0)	
3c	−3.50	4107	−4.91	1827	17		
4a	18.43	4219	15.64	1611	22		
4b	18.94	4206	13.73	1633	22		
4c	17.34	4040	10.12	1670	22		
5a	44.14	4191	47.56	1678	11		
5b	44.71	4170	46.88	1680	11		
5c	43.85	4006	45.29	1684	12		
6a	13.77	4158	11.03	1749	25	2.5 (5.0)	
7a	13.63	4112	13.63	1824	24		
6b, **7b**	12.86	4151	8.78	1756	26	1.5 (5.0)	
	13.62	4113	12.42	1842	24		
6c, **7c**[c]	8.62	4000	5.06	1678	26	1.0 (5.0)	
	10.42	3976	9.89	1867	24		
8a, **9a**	42.60	4169	43.38	1883	14	1.0 (1.0)	
	43.27	4109	43.47	1855	14		
8b, **9b**	43.25	4098	42.54	1845	14	1.0 (1.0)	
	42.80	4143	42.55	1874	14		
8c, **9c**[c]	41.04	3940	41.17	1833	13	1.0 (1.0)	
	40.60	3987	40.64	1857	13		
10a, **11a**[c]	3.34	4280	1.29	1866	17	1.5	
	2.04	4448	2.58	1811	18		
10b, **11b**[d]	4.18	4256	−1.82	1828	18	1.0	
	2.04	4237	0.68	1864	17		
10c, **11c**[d]	0.11	4109	−7.77	1823	18	1.0	
	−2.51	4087	−4.24	1884	17		
12a, **13a**	5.61	4316	4.34	1770	16	4.0 (4.0)	
	2.28	4248	3.63	1760	17		
12b, **13b**[e]	4.57	4285	1.82	1839	17	4.0 (4.0)	
	1.51	4201	0.77	1817	17		
12c, **13c**	0.52	4113	−2.90	1811	16	1.5 (4.0)	
	1.61	3915	−2.84	1930	16		
14a, **15a**	5.43	4269	3.55	1766	16	2.5 (2.0)	
	3.69	4306	2.37	1762	17		
14b, **15b**[d]	4.58	4247	0.10	1819	17	2.0 (2.0)	
	2.87	4278	−0.78	1811	18		
14c, **15c**	0.81	4064	−3.90	1824	16	2.5 (2.0)	
	−2.59	4105	−5.96	1780	17		
16b, **17b**	8.54	2440	8.54	1804	11	nr	
16c, **17c**	9.49	2483	7.39	1801	11	12	−205
	8.48	2461	7.78	1783	11		−199
18c, **19c**	9.72	2463	7.84	1783	11	n.r.	−235
20c, **21c**	9.33	2454	7.45	1778	11	10	−208, −238
22a, **23a**	8.92	2527	9.98	1811	10	nr	
22b, **23b**	9.46	2560	9.31	1804	11	nr	
22c, **23c**	11.10	2609	7.89	1812	11	25	−207, 218
24c, **25c**[f]	19.11	2458	14.25	1707	19	nr	
26c, **27c**[f]	47.85	2413	47.97	1768	10	1.0	
	46.58	2393	46.11	1737	10		
28	130.28	4531	52.47	1753	10		
29	151.14	1987	51.12	4224	10		
30	50.44	4214	143.92	2158	15		
31	131.07	4482	50.44	1948	10		

[a] ^{31}P (81 MHz) and ^{195}Pt (85 MHz) NMR spectra were measured in $CDCl_3$ at 28 °C unless otherwise stated. Chemical shifts (δ) are in ppm (±0.1) to high frequency of 85% H_3PO_4 or $\Xi(Pt) = 21.4$ MHz. Coupling constants (J) are 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); values in parentheses are ratios determined in MeCN instead of $CDCl_3$. nr = not resolved, because either the signals for the minor isomer are too weak or they are coincident with those of the major isomer. [c] In CH_2Cl_2 (C_6D_6 in a capillary as lock). [d] In DMSO (C_6D_6 in a capillary as lock). [e] In a 1:1 CH_2Cl_2/MeCN mixture (C_6D_6 in a capillary as lock). [f] In C_6D_6

A mixture of **16c** and **17c** was isolated from benzene, and their structures were assigned on the basis of elemental analysis, IR, ^{1}H, and especially ^{31}P and ^{195}Pt NMR (see Table 1 and Experimental Section), though the absolute stereochemistry is unknown. The related complexes derived from *l*-menthyl diazoacetate (**18c**, **19c**; **20c**, **21c**) and diazoacetophenone (**22c**, **23c**) have been isolated and characterized (see Table 1 and Experimental Section). In each of the Pt–I insertion reactions studied, where the diastereoisomers have been observed, the diastereoselectivity is high (see Table 1); e.g., for the acetophenone derivatives **22c** and **23c** the ratio of diastereoisomers is *ca.* 25:1.

Complexes **2c** and **3c** are the products of insertion of $CHCO_2Et$ into the Pt–C bonds of **1c**, and complexes **16c** and **17c** are the products of insertion of $CHCO_2Et$ into the Pt–I bonds of **1c**. As in the diastereoselectivity study above, the effects of solvent, halogen ligand,

Scheme 2

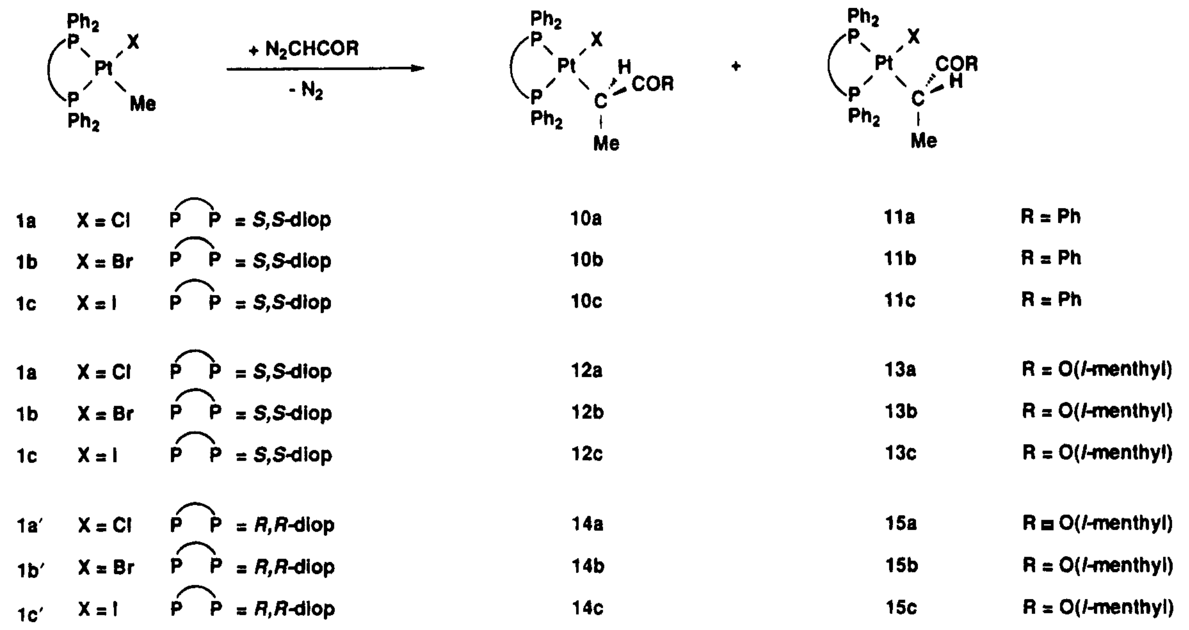


Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

Pt(1)–Pt(1)	2.227(4)	Pt(1)–P(2)	2.331(4)	Pt(1)–Cl(1)	2.364(4)
Pt(1)–C(8)	2.171(14)	P(1)–C(1)	1.844(19)	P(1)–C(21)	1.808(17)
P(1)–C(31)	1.819(13)	P(2)–C(4)	1.855(15)	P(2)–C(41)	1.836(16)
P(2)–C(51)	1.843(15)	C(1)–C(2)	1.533(25)	C(2)–C(3)	1.494(19)
C(2)–O(1)	1.416(17)	C(3)–C(4)	1.471(20)	C(3)–O(2)	1.456(20)
O(1)–C(5)	1.431(24)	O(2)–C(5)	1.465(19)	C(5)–C(6)	1.487(29)
C(5)–C(7)	1.504(33)	C(8)–C(9)	1.552(21)	C(8)–C(10)	1.507(21)
C(10)–O(3)	1.195(20)	C(10)–O(4)	1.357(20)	O(4)–C(11)	1.454(22)
C(11)–C(12)	1.421(30)				

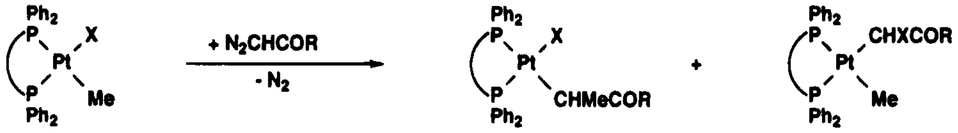
P(1)–Pt(1)–P(2)	100.1(1)	P(1)–Pt(1)–Cl(1)	167.4(2)
P(2)–Pt(1)–Cl(1)	86.5(1)	P(1)–Pt(1)–C(8)	87.2(4)
P(2)–Pt(1)–C(8)	172.6(4)	Cl(1)–Pt(1)–C(8)	86.4(4)
Pt(1)–P(1)–C(1)	118.6(6)	Pt(1)–P(1)–C(21)	110.1(5)
C(1)–P(1)–C(21)	102.0(8)	Pt(1)–P(1)–C(31)	116.9(4)
C(1)–P(1)–C(31)	102.4(7)	C(21)–P(1)–C(31)	105.0(7)
Pt(1)–P(2)–(C4)	123.2(5)	Pt(1)–P(2)–C(41)	112.5(6)
C(4)–P(2)–C(41)	104.5(7)	Pt(1)–P(2)–C(51)	111.0(5)
C(4)–P(2)–C(51)	96.5(7)	C(41)–P(2)–C(51)	107.2(7)
P(1)–C(1)–C(2)	112.8(12)	C(1)–C(2)–C(3)	114.5(14)
C(1)–C(2)–O(1)	106.4(14)	C(3)–C(2)–O(1)	103.6(11)
C(2)–C(3)–C(4)	119.9(13)	C(2)–C(3)–O(2)	102.7(11)
C(4)–C(3)–O(2)	109.5(14)	P(2)–C(4)–C(3)	121.4(12)
C(2)–O(1)–C(5)	106.4(13)	C(3)–O(2)–C(5)	105.7(13)
O(1)–C(5)–O(2)	107.2(13)	O(1)–C(5)–C(6)	107.6(19)
O(2)–C(5)–C(6)	107.4(14)	O(1)–C(5)–C(7)	114.5(16)
O(2)–C(5)–C(7)	106.5(18)	C(6)–C(5)–C(7)	113.3(18)
Pt(1)–C(8)–C(9)	109.9(10)	Pt(1)–C(8)–C(10)	108.4(10)
C(9)–C(8)–C(10)	113.7(12)	C(8)–C(10)–O(3)	125.1(14)
C(8)–C(10)–O(4)	110.8(13)	O(3)–C(10)–O(4)	124.1(15)
C(10)–O(4)–C(11)	117.1(13)	O(4)–C(11)–C(12)	111.8(17)

diphosphine ligand, and diazo carbonyl reagent on the chemoselectivity for Pt–C or Pt–X insertion have been explored. The reactions shown in Scheme 3 were followed by ^{31}P NMR spectroscopy (see Table 1 for the data). In general, products derived from Pt–C and Pt–X insertion were observed and their relative proportions estimated by integration of the ^{31}P NMR signals. From the results collected in Table 3, it can be seen that the following trends in the proportion of Pt–C insertion products formed are discernible: (1) $C_6D_6 < CDCl_3 < CD_2Cl_2 < (CD_3)_2SO$; (2) I < Br < Cl; (3) diop < skewphos, chiraphos; (4) $N_2CHCOPh < N_2CHCO_2Et$.

The proportion of product derived from Pt–C insertion, in the reaction of N_2CHCO_2Et with the bromo complex **1b** in $CDCl_3$, increased at lower temperatures (65% at +60 °C, 80% at +20 °C, 90% at −15 °C); i.e., this reaction is more chemoselective at lower temperatures.

Mechanistic Considerations. When [PtI(CH$_3$)(*S*,*S*-diop)] (**1c**) is treated with $N_2CHCOPh$ in DMSO or MeCN, the Pt–C and Pt–I insertion products **10c**, **11c** and **22c**, **23c** are formed rapidly and simultaneously, in the ratio *ca.* 4:1. The isolated, pure mixture of **22c** and **23c** redissolved in DMSO or MeCN does not isomerize to **10c**, **11c** over a period of 14 days. Similarly, no isomerization is observed when any of the other Pt–I insertion products **16c**–**21c** are dissolved in MeCN or DMSO.[8] This demonstrates that (i) the Pt–I insertion products are not intermediates in the formation of Pt–C insertion products and therefore they are formed

Scheme 3



1a	X = Cl	P⌒P = S,S-diop	2a, 3a		R = OEt
1b	X = Br	P⌒P = S,S-diop	2b, 3b	16b, 17b	R = OEt
1c	X = I	P⌒P = S,S-diop	2c, 3c	16c, 17c	R = OEt
1c	X = I	P⌒P = S,S-diop	12c, 13c	18c, 19c	R = O(*l*-menthyl)
1c′	X = I	P⌒P = R,R-diop	14c, 15c	20c, 21c	R = O(*l*-menthyl)
1a	X = Cl	P⌒P = S,S-diop	10a, 11a	22a, 23a	R = Ph
1b	X = Br	P⌒P = S,S-diop	10b, 11b	22b, 23b	R = Ph
1c	X = I	P⌒P = S,S-diop	10c, 11c	22c, 23c	R = Ph
4c	X = I	P⌒P = S,S-skewphos	6c, 7c	24c, 25c	R = OEt
5c	X = I	P⌒P = S,S-chiraphos	8c, 9c	26c, 27c	R = OEt

by parallel mechanisms and (ii) the chemoselectivity of the insertions is under kinetic control.

We propose the mechanism in Scheme 4 for the Pt–C insertion in polar solvents; it consists of nucleophilic substitution of halide by the diazo carbonyl to form the cationic intermediate **A** (step i) and then migration of the methyl group to form the new C–C bond, promoted either by recoordination of the halide (step ii) or by coordination of solvent (step iii) followed by halide substitution (step iv).[9] Intermediate **A** has canonical forms $\mathbf{A_1}$ and $\mathbf{A_2}$, and the C–C bond-forming step from **A** can be viewed in two valid ways (Scheme 5): (a) as an alkyl to carbene migration which emphasizes form $\mathbf{A_1}$ where the driving force is the formation of the strong C–C bond or (b) as a Wagner–Meerwein-like rearrangement of the carbonium ion, which emphasizes the alternative canonical form $\mathbf{A_2}$ where the driving force is the formation of a more stable cation. McCrindle et al.[10a] have proposed an alkyl to carbene migration in a cationic platinum(II) complex in the [PtCl(CH$_3$)(COD)]-catalyzed polymerization of CH_2N_2, and Stryker et al.[3a] have described an ylide to carbene migration as a step in a platinum-mediated synthesis of (oxapentylidene)-triphenylphosphonium tetrafluoroborate. Moreover, it has been shown that alkyl to carbene migration occurs particularly readily when the complex is cationic.[10]

Table 3. Ratio of Pt–C to Pt–X Insertion Products Formed in the Reaction of [PtX(CH$_3$)(diphos)] with N$_2$CHCOR in Various Solvents Expressed as a Percentage[a]

X	R	diphos	$(CH_3)_2SO$	CH_2Cl_2	$CHCl_3$	C_6H_6
Cl	Ph	*S,S*-diop	100	80	65	0
Br	Ph	*S,S*-diop	100	65	10	0
I	Ph	*S,S*-diop	80	0	0	0
Cl	EtO	*S,S*-diop	100	100	100	100
Br	EtO	*S,S*-diop	100	80	80	45
I	EtO	*S,S*-diop	100	60	55	15
I	EtO	*S,S*-skew	100	100	nd	80
I	EtO	*S,S*-chiraphos	100	100	nd	85

[a] The percentages are estimated from integration of the ^{31}P signals with an error of *ca.* 5%. Values of 100 or 0 indicate that only one isomer was detected in the ^{31}P NMR spectrum, implying that there was less than *ca.* 2% of the other isomer present. nd = not determined.

The intermediacy of **A** in the Pt–C insertion reaction (Scheme 4) can be used to rationalize the following observations:

(1) Solvents that would promote the formation of an ionic intermediate **A** (i.e. polar solvents of high dielectric constant) promote Pt–C insertion.

(2) The order of increasing nucleofugacity from platinum(II) ($I < Br < Cl$)[11] is the same as the order of increasing tendency to Pt–C insertion because the better the leaving group, the easier the formation of intermediate **A**.[12]

(3) In DMSO or MeCN, the diastereomeric ratio of Pt–C insertion products is independent of the halogen

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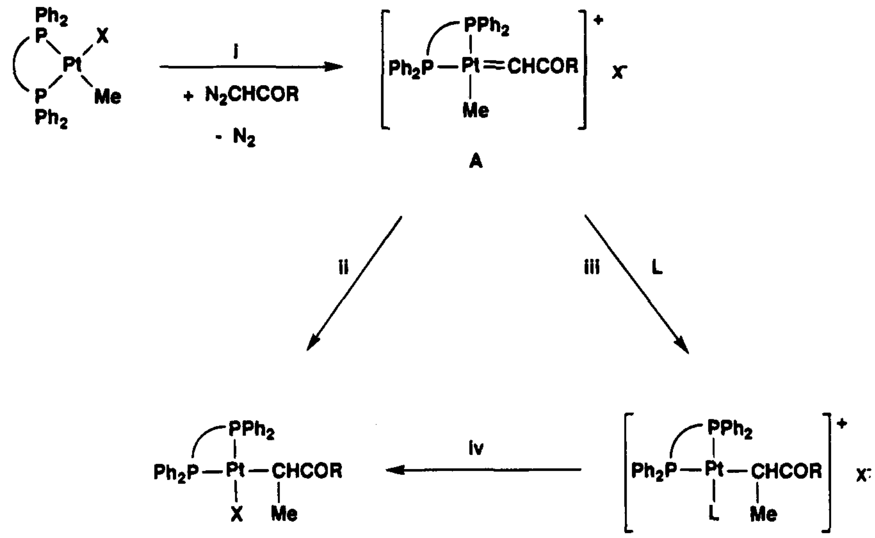
[8] Addition of AgX (X = PF$_6$, CF$_3$SO$_3$) to the Pt–I insertion products **16c**–**23c** promoted the migration of the Me group from Pt to C quantitatively, as shown by ^{31}P NMR spectroscopy (see Experimental Section). It is tempting to suggest that addition of Ag$^+$ yields a cationic carbene complex (such as A in Scheme 4) and Me migration then occurs rapidly. However, this inference is obfuscated by the observation that the diastereomeric ratios obtained by this Ag$^+$-promoted route are very different (see Experimental Section) from those obtained by direct insertions (Schemes 1 and 2). One plausible explanation of this behavior is that an intermediate iodocarbon–silver(I) complex is involved, but extensive further work would be required to elucidate this point.

[9] The possibility that methyl migration takes place within the diazoalkane complex intermediate [PtMe(N$_2$CHR)(diphosphine)]$^+$ has also been explored using ^{31}P NMR. It was reasoned that such an intermediate would be more readily formed by treatment of the labile complex [PtMe(NCMe)(*S,S*-diop)][O$_3$SCF$_3$] with N$_2$CHCO$_2$R (R = Et, *l*-menthyl). This procedure (see Experimental Section) yielded the complexes [Pt(CHMeCO$_2$R)(NCMe)(*S,S*-diop)][O$_3$SCF$_3$] rapidly and quantitatively, as shown by their independent synthesis upon treatment of the corresponding [PtCl(CHMeCO$_2$R)(*S,S*-diop)] mixture with AgO$_3$SCF$_3$. However, the ratios of diastereoisomers obtained from the MeCN complexes were different (see Experimental Section) from those obtained with the halide complexes (Scheme 1), from which it was deduced that Me migration within a diazoalkane complex does not make a major contribution to the reactions in Scheme 1.

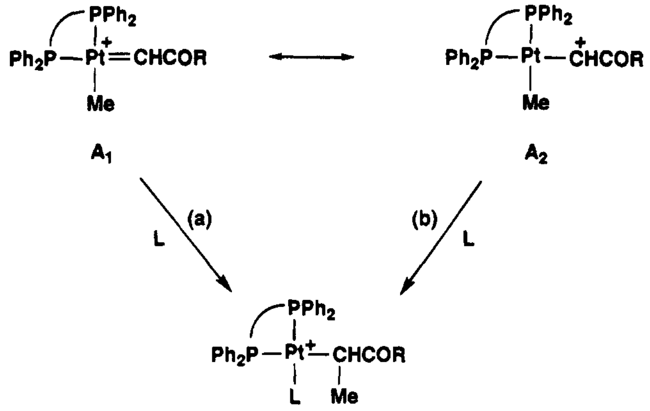
[10] (a) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (c) Hubbard, J. L.; Morneau, A.; Burns, R. M.; Nadeau, O. W. *J. Am. Chem. Soc.* **1991**, *113*, 9180.

[11] Tobe, M. L. *Inorganic Reaction Mechanisms*; Nelson: London, 1972.

Scheme 4



Scheme 5



for each of the reactions shown in Schemes 1 and 2, as expected if the halogen is lost to give intermediate **A**.

(4) The geometric isomers **28** and **29** (see Scheme 6) are available as 1:1 and a 1:3 mixtures (see Experimental Section). Treatment of these mixtures with N_2CHCO_2Et in $CDCl_3$ gave a 1:1 and 1:3 mixture of the products **30** and **31**, respectively, as shown unambiguously by ^{31}P NMR spectroscopy (see Table 1 and Experimental Section for the characterization data). These observations are consistent with **28** giving **30** and **29** giving **31** (Scheme 6), and therefore these reactions involve an inversion of configuration at the platinum. This is precisely what would be predicted from the mechanism in Scheme 4. Substitution of the chloride in **28** would give a cationic species similar to **A** from which the product **30** would be formed by methyl migration and chloride recoordination (as in Scheme 6). Using the same reasoning, **31** would be the predicted product from **29**.

Though investigation of the Pt−C insertions was the principal thrust of this work, we have also considered the Pt−X insertions that occur simultaneously. The factors that promote Pt−X insertion, which are (see above) (a) nonpolar solvents, (b) I > Br > Cl, (c) diop rather than skewphos or chiraphos complexes, and (d) $N_2CHCOPh$ rather than N_2CHCO_2R, can be largely accounted for by the unified mechanism shown in Scheme 7. It is proposed that Pt−X insertion occurs directly from a neutral, trigonal-bipyramidal carbene complex such as **B**.[13] Therefore, Pt−X insertion should be favored by factors that stabilize **B** relative to the cationic carbene **A**. Clearly, nonpolar solvents would relatively stabilize neutral species **B**. Iodide is well-known to stabilize five-coordinate platinum(II),[14] and the equatorial angle of 120° will be more easily spanned by diop than by skewphos or chiraphos.[15] Explanations for the effect of the diazo carbonyl reagent on the chemoselectivity and the observed high diastereoselectivity for the Pt−X insertions (Table I) remain elusive.

It had been previously noted (see above) that the ratio of diastereoisomers from the reaction of $[PtX(CH_3)$(chiral diphos)] was independent of halogen X when the reaction was carried out in MeCN or DMSO, but this was no longer true when the reactions were carried out in less polar solvents. This suggests that, in nonpolar solvents, the halogen is coordinated at the C−C bond-forming step, indicating that some Pt−C insertion may derive from methyl migration within a neutral intermediate such as **B** (Scheme 7).[13]

Conclusion. It has been demonstrated that a new C−C bond can be diastereoselectively created within the coordination sphere of platinum(II) by the insertion of a substituted carbene into a Pt−C bond. While the factors that control the chemoselectivity (Pt−C versus Pt−X) are well understood, the diastereoselectivity of these reactions is not a simple function of substrate or diazo reagent and is influenced strongly by solvent effects.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen, though the products could be handled in air. CH_2-

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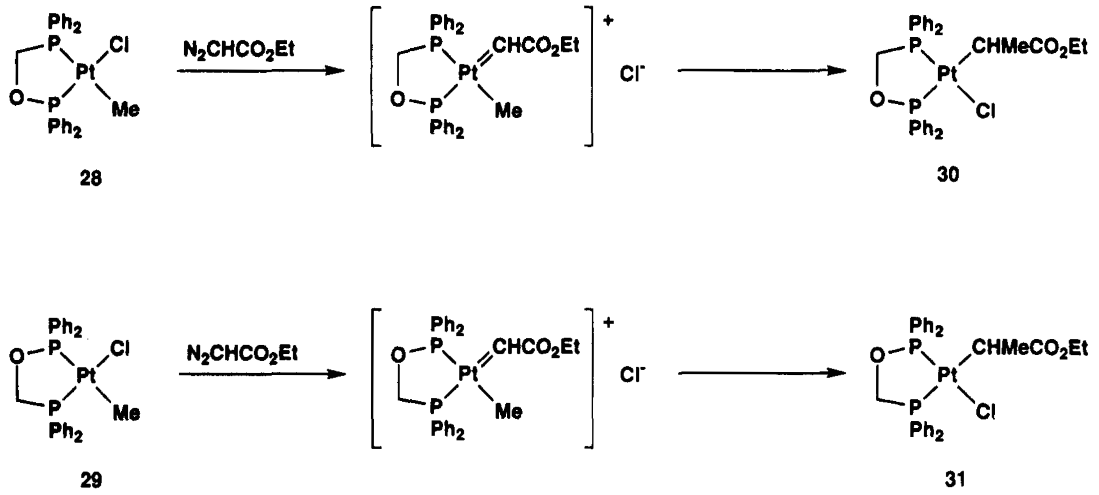
(12) No reaction took place between $[Pt(CH_3)_2(R,R\text{-diop})]$ and N_2CHCO_2Et in $CDCl_3$ even after reflux for 2 h, consistent with the requirement for a labile group on the platinum.

(13) It is possible that a proportion of the Pt−X insertion products and the Pt−C insertion products in nonpolar solvents are derived from diazoalkane complexes such as **C** (Scheme 7), since the features discussed here that should stabilize **B** would also stabilize **C**. The distinction between routes via **B** and **C** is a question of whether migration of X or Me is synchronous with N_2 loss. It has previously been suggested that, in nonpolar solvents, complexes of the type $[Pt(CH_3)(CHCl_2)(dppe)]$ rearrange by alkyl migration to $[PtCl(CHClCH_3)(dppe)]$; see: van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243.

(14) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.

(15) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *117*, 5535.

Scheme 6



Cl_2 was distilled from CaH_2 under nitrogen. All the diphosphines (Aldrich) and N_2CHCO_2Et (Fluka) were used as purchased, and N_2CHCO_2(*l*-menthyl),[16] $N_2CHCOPh$,[17] and [$PtX(CH_3)$(COD)] (COD = 1,5-cyclooctadiene; X = Cl, Br, I)[18] were made by literature methods. FT-IR spectra were obtained using a Nicolet 510P spectrometer. ^{31}P (81 MHz) and ^{1}H NMR spectra were measured in $CDCl_3$ at +22 °C using a Bruker AM200 spectrometer (200 MHz) or at +25 °C using a Varian Gemini 300 spectrometer (300 MHz). ^{195}Pt NMR spectra were measured at 85.6 MHz in $CDCl_3$ at 25 °C using a JEOL GX400 spectrometer; chemical shifts (δ) are to high frequency of 85% H_3PO_4, $Si(CH_3)_4$, or Ξ(Pt) = 21.4 MHz.

Preparation of [PtI(CH₃)(*S*,*S*-diop)] (1c). A solution of 179 mg (0.36 mmol) of *S*,*S*-diop in 20 mL of CH_2Cl_2 was added dropwise over 30 min to a solution of 160 mg (0.36 mmol) of [$PtI(CH_3)$(COD)] in 30 mL of CH_2Cl_2, and the mixture was stirred for 1 h. The solvent was then stripped under reduced pressure, and the yellow solid product (277 mg, 92%) was triturated with 5 mL of Et_2O and then filtered off. All the complexes **1a–c**, **4a–c**, and **5a–c** were made similarly in yields of 85–90%.

Preparation of [PtCl(CHMeCO₂Et)(*S*,*S*-diop)] (2a, 3a). A 1.4 mL amount of a 0.438 M solution of N_2CHCO_2Et (0.6 mmol) in CH_2Cl_2 was added to a solution of 200 mg (0.27 mmol) of [$PtCl(CH_3)$(*S*,*S*-diop)] in 8 mL of CH_2Cl_2 and the mixture stirred for 16 h. The solution was then evaporated to 0.5 mL and 15 mL of *n*-pentane added to precipitate the white solid product (182 mg, 82%). The isomer **2a** was crystallized by layering a CH_2Cl_2 solution of the mixture of **2a** and **3a** with Et_2O. Characterization data for **2a** and **3a** (see Table 1 for ^{31}P NMR) are as follows. Anal. Found (calcd) for $C_{36}H_{41}ClO_4P_2Pt{\cdot}CH_2Cl_2$: C, 48.65 (48.55); H, 4.80 (4.75). IR (CsI pellet): ν(CO) 1701 (s), ν(PtCl) 290 (m) cm^{-1} ^{1}H NMR ($CDCl_3$) for **2a**: δ 0.66 ($^{3}J_{Pt-H}$ = 32.6 Hz, $^{3}J_{H-H}$ = 7.7 Hz, $^{4}J_{P-H}$ = 7.7 Hz, 3H, $PtCHCH_3$), 2.15 (assigned from COSY to $PtCHCH_3$). ^{13}C NMR ($CDCl_3$) for **2a**: δ 15.3 ($^{2}J_{Pt-C}$ = 57.6 Hz, $PtCHCH_3$), 32.0 (assigned from DEPT to $PtCHCH_3$). ^{1}H NMR ($CDCl_3$) for **3a**: δ 0.9 ($^{3}J_{Pt-H}$ not resolved, $^{3}J_{H-H}$ = 7.5 Hz, $^{4}J_{P-H}$ = 7.5 Hz, 3H, $PtCHCH_3$).

The following were made similarly: **6a**, **7a** (67%), **8a**, **9a** (67%), **12a**, **13a** (62%), **14a**, **15a** (68%). Elemental analysis and IR (CsI disk) data are as follows. **6a**, **7a**: Anal. Found (calcd for $C_{33}H_{37}ClO_2P_2Pt{\cdot}0.25CH_2Cl_2$): C, 51.25 (51.25); H, 5.15 (4.80). ν(CO): 1695 (s) cm^{-1}. **8a**, **9a**: Anal. Found (calcd for $C_{32}H_{35}ClO_2P_2Pt{\cdot}0.25CH_2Cl_2$): C, 51.05 (50.65); H, 5.00 (4.65). ν(CO): 1688 (s) cm^{-1}. **12a**, **13a**: Anal. Found (calcd for $C_{45}H_{53}ClO_4P_2Pt{\cdot}0.75CH_2Cl_2$): C, 53.95 (54.15); H, 5.75 (5.45). ν(CO): 1701 (s) cm^{-1}. **14a**, **15a**: Anal. Found (calcd for $C_{44}H_{55}ClO_4P_2Pt{\cdot}0.25CH_2Cl_2$): C, 54.90 (55.25); H, 5.90 (5.80). ν(CO): 1696 (s) cm^{-1}. The configuration of the α-carbon in **6a** was determined to be *R* by adding skewphos (1 equiv) to a $CDCl_3$ solution of pure **2a**, and after 5 h the formation of **6a** (and no **7a**) was detected by ^{31}P NMR spectroscopy.

Preparation of [PtBr(CHMeCO₂Et)(*S*,*S*-diop)] (2b, 3b) and [PtI(CHMeCO₂Et)(*S*,*S*-diop)] (2c, 3c). Procedure A. A 1.0 mL portion of a 0.438 M solution of N_2CHCO_2Et (0.44 mmol) in CH_2Cl_2 was added to a solution of 165 mg (0.21 mmol) of [PtBrMe(*S*,*S*-diop)] in 4 mL of MeCN, and the mixture was stirred for 3 h. The solution was then evaporated to dryness to leave a colorless oil. Addition of 2 mL of Et_2O and 15 mL of *n*-pentane gave the white solid product (140 mg, 76%). Characterization data for **2b**, **3b** are as follows. Anal. Found (calcd for $C_{36}H_{41}BrO_4P_2Pt{\cdot}CH_2Cl_2$): C, 49.65 (49.45); H, 4.85 (4.70). IR (CsI pellet): ν(CO) 1701 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) for **2b**: δ 0.64 ($^{3}J_{Pt-H}$ = 34.4 Hz, $^{3}J_{H-H}$ = 7.7 Hz, $^{4}J_{P-H}$ = 7.7 Hz, 3H); it was not possible to assign any other signals because of the complex overlapping multiplets associated with diop resonances in the δ 1–4 region.

Procedure B. A solution of 174 mg (2.0 mmol) of LiBr in 1 mL of MeCN was added to a solution of 166 mg (0.20 mmol) of [$PtCl(CHMeCO_2Et)$(*S*,*S*-diop)] in 1 mL of CH_2Cl_2 and 4 mL of MeCN, and the mixture was stirred at ambient temperature for 1 h. The solvent was then removed under reduced pressure, water and CH_2Cl_2 were added, and the organic layer was separated, dried over Na_2SO_4, and then reduced to dryness. Trituration of the residue with Et_2O gave the white solid product (150 mg, 81%).

The iodo species **2c** and **3c** can be made similarly by either procedure A or B, but the product was always contaminated with small amounts (5–10%) of [PtI_2(*S*,*S*-diop)] and other decomposition products and was not obtained in pure form (see Table 1 for ^{31}P NMR data). The bromo complexes **6b–9b** and **12b–15b** and the iodo complexes **6c–9c** and **12c–15c** were made by procedure A and characterized in solution only by ^{31}P NMR (see Table 1).

Preparation of [PtMe(CHICO₂Et)(*S*,*S*-diop)] (16c, 17c). A solution of 80 mg (0.70 mmol) of N_2CHCO_2Et in 1 mL of C_6H_6 was added to a solution of 180 mg (0.21 mmol) of [PtIMe-(*S*,*S*-diop)] in 4 mL of C_6H_6 and the mixture stirred for 4 h. The solution was then evaporated to dryness to give a yellow oil, and 2 mL of Et_2O and 15 mL of *n*-pentane were added to give the off-white solid product (120 mg, 62%). Characterization data for **16c**, **17c** are as follows. Anal. Found (calcd for $C_{36}H_{41}IO_4P_2Pt{\cdot}0.75CH_2Cl_2$): C, 44.85 (44.75); H, 4.35 (4.30). IR (CsI pellet): ν(CO) 1709 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.50 ($^{3}J_{Pt-H}$ = 63.3 Hz, 3H, $PtCH_3$). The following were made similarly: **18c**, **19c** (71%), **20c**, **21c** (70%), **22c**, **23c** (62%) (made in CH_2Cl_2). ^{31}P and ^{195}Pt NMR data are given in Table 1 but the ^{1}H NMR spectra of these complexes were uninforma-

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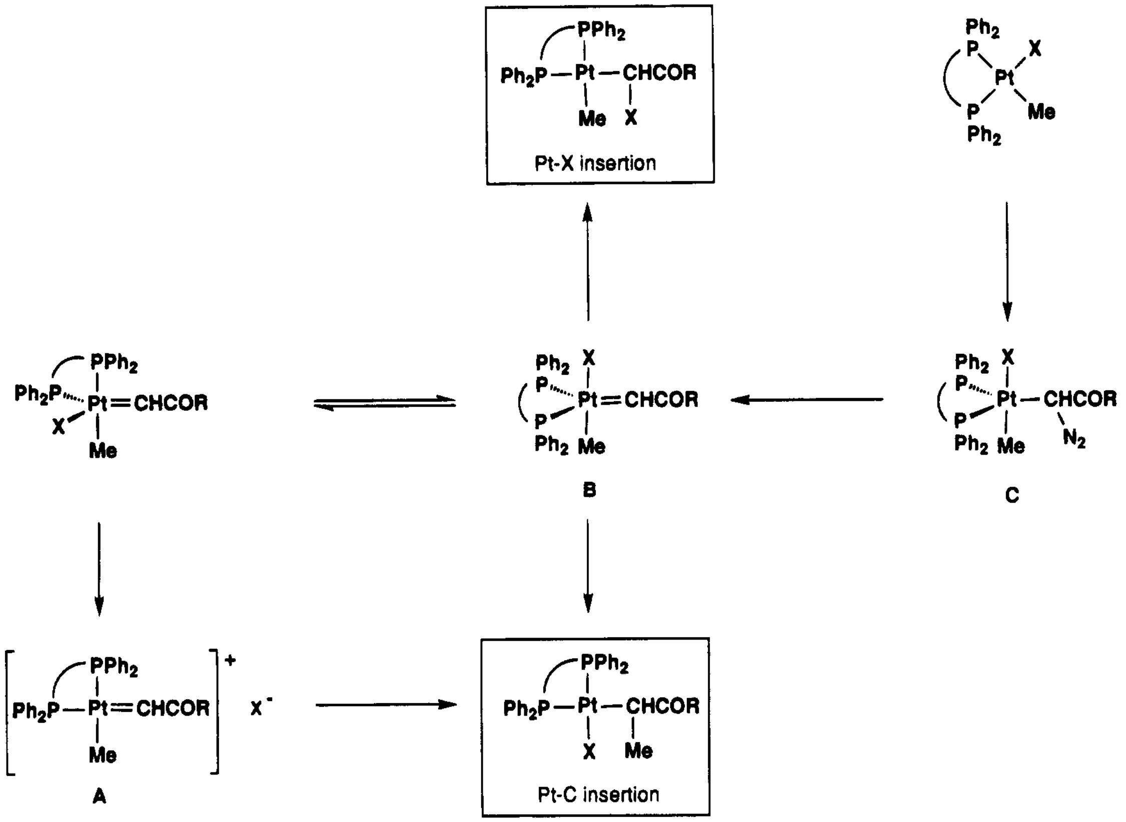
(16) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553.

(17) Scott, L. T.; Minton, M. A. *J. Org. Chem.* **1977**, *42*, 3757.

(18) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

Scheme 7



tive because the PtCHMe signals were obscured by the diop and menthyl resonances. Elemental analysis and IR (CsI disk) data are as follows. **18c**, **19c**: Anal. Found (calcd for $C_{44}H_{55}IO_4P_2Pt{\cdot}CH_2Cl_2$): C, 48.65 (48.35); H, 5.10 (5.25). ν(CO): 1702 (s) cm^{-1}. **20c, 21c**: Anal. Found (calcd for $C_{44}H_{55}IO_4P_2Pt{\cdot}0.5CH_2Cl_2$): C, 49.65 (49.70); H, 5.40 (5.35). ν(CO): 1705 (s) cm^{-1}. **22c, 23c**: Anal. Found (calcd) for $C_{40}H_{41}IO_3P_2Pt$): C, 50.60 (50.35); H, 4.30 (4.30). ν(CO): 1651 (s) cm^{-1}.

Reaction of *rac*-[PtCl(CH$_3$)(diop)] with *l*-Menthyl Diazoacetate. To a mixture of 20 mg (0.027 mmol) of [PtCl(CH$_3$)(*S*,*S*-diop)] and 20 mg (0.027 mmol) of [PtCl(CH$_3$)(*R*,*R*-diop)] dissolved in 0.4 mL of $CDCl_3$ in an NMR tube was added 6 mg (0.027 mmol) of *l*-menthyl diazoacetate and the progress of the reaction followed by measuring the ^{31}P NMR spectrum at regular intervals. The reaction was complete after 10 h.

NMR Reactions To Determine Chemoselectivity/Diastereoselectivity. In a typical experiment a solution of 0.025 mmol of platinum substrate [PtX(CH$_3$)(*S*,*S*-diop)] in 0.4 mL of solvent (DMSO, CH_2Cl_2, $CHCl_3$, C_6H_6) in an NMR tube (containing a capillary tube of C_6D_6 for lock) was treated with 0.025 mmol of a 0.438 M solution of N_2CHCO_2Et in the same solvent and the mixture shaken. All other combinations of reagents shown in Table 3 were studied in the same way.

Preparation of [PtClMe(Ph$_2$PCH$_2$OPPh$_2$)] (28, 29). A solution of 89 mg (0.27 mmol) of [Pt(CH$_3$)$_2$(COD)] in 25 mL of dry, deoxygenated CH_2Cl_2 was cooled to −20 °C, and then 59 mg (0.27 mmol) of Ph_2PCH_2OH and 50 μL (0.28 mmol) of Ph_2PCl were added in rapid succession. The resulting solution was stirred for 1 h, and then the solution was warmed slowly to room temperature. The solution was then concentrated to 1−2 mL, and 50 mL of Et_2O was added to precipitate the white solid product, which was filtered off in air and washed with 5 mL of Et_2O. The product (113 mg, 65%) was a 1:1 mixture of geometric isomers **28** and **29**. The filtrate comtained a 1:3 mixture of **28** and **29**, respectively. Anal. Found (calcd for $C_{26}H_{25}ClOP_2Pt$): C, 48.40 (48.35); H, 3.90 (3.90). IR (CsI pellet): ν(PtCl) 295 (m) cm^{-1}.

Preparation of [PtCl(CHMeCO$_2$Et)(Ph$_2$PCH$_2$OPPh$_2$)] (30, 31). A 48 μL (0.46 mmol) portion of N_2CHCO_2Et was added to a suspension of a 1:1 mixture of **28** and **29** in 0.7 mL of CD_2Cl_2 in an NMR tube. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 4 h the reaction was complete and the yellow solution was added to 20 mL of *n*-pentane to precipitate the white solid mixture of isomers **30** and **31** (81 mg, 75%), which was filtered off and washed with 5 mL of *n*-pentane. Anal. Found (calcd for $C_{30}H_{31}ClO_3P_2Pt$): C, 49.00 (49.20); H, 4.35 (4.30). IR (CsI pellet): ν(PtCl) 305 (m) cm^{-1}; ν(CO) 1695(s), 1670(s) cm^{-1}.

Reaction of [PtMe(CHICO$_2$Et)(*S*,*S*-diop)] with Silver Salts. A 6.8 mg (0.027 mmol) amount of AgO_3SCF_3 was added to a solution of 25 mg (0.027 mmol) of [PtMe(CHICO$_2$Et)(*S*,*S*-diop)] in 0.5 mL of a 1:1 mixture of CH_2Cl_2 and MeCN. After 5 min the solution was filtered free of the pale yellow AgI precipitate and the product examined by ^{31}P NMR spectroscopy. Addition of 25 mg (0.057 mmol) of [AsPh$_4$]Cl·H$_2$O to the solution generated **2a** and **3a** exclusively. The results were exactly the same when $AgPF_6$ or $AgBF_4$ was used in place of silver triflate. Similar experiments were carried out between silver salts and [PtMe(CHICO$_2$R*)(*S*,*S*-diop)] or (PtMe(CHICO$_2$R*)(*R*,*R*-diop)] (R* = *l*-menthyl). In each of these experiments, the ratio of the diastereomeric products differed significantly from those obtained via the route shown in Scheme 1. The ratios of the products were as follows (ratios obtained via Scheme 1 shown in parentheses for comparison): **2a**, **3a**, 1:2 (2:1); **12a**, **13a**, 1:1 (4:1); **14a**, **15a**, 1:4 (2:1).

Reaction of [PtMe(NCMe)(*S*,*S*-diop)][O$_3$SCF$_3$] with N$_2$CHCO$_2$Et. A solution of 25 mg (0.034 mmol) of [PtCl(CH$_3$)(*S*,*S*-diop)] in 0.4 mL of MeCN (C_6D_6 capillary for lock) was treated with 12 mg (0.034 mmol) of AgO_3SCF_3 (identical results were obtained when $AgBF_4$ was used). After 5 min, the resulting suspension was filtered free of AgCl and then 0.034 mmol of a 0.438 M solution of N_2CHCO_2Et in MeCN was added; the products were assigned by ^{31}P NMR spectroscopy to diastereoisomers of [Pt(CHMeCO$_2$Et)(NCMe)(*S*,*S*-diop)][O$_3$SCF$_3$]. (Precisely the same products were obtained upon treatment of [PtCl(CHMeCO$_2$Et)(*S*,*S*-diop)] (**2a** and **3a**) with AgO_3SCF_3 in MeCN). Addition of 15 mg (0.034 mmol) of [AsPh$_4$]Cl to the solutions of [Pt(CHMeCO$_2$Et)(NCMe)(*S*,*S*-diop)][O$_3$SCF$_3$] gave the familiar resonances for **2a** and **3a**,

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)

atom	*x*	*y*	*z*	U_{eq}[a]
Pt(1)	2634(1)	2197(1)	1965(1)	39(1)
P(1)	3119(2)	1217(2)	2379(4)	38(1)
P(2)	2360(3)	2552(2)	4020(4)	43(1)
Cl(1)	2399(3)	3273(2)	1315(4)	65(2)
C(1)	3322(11)	995(9)	4043(18)	68(6)
C(2)	2546(11)	907(6)	4823(14)	54(5)
C(3)	2368(12)	1447(6)	5721(13)	56(5)
C(4)	1932(10)	2022(6)	5271(15)	52(5)
O(1)	2684(10)	373(5)	5635(10)	78(5)
O(2)	1897(10)	1131(5)	6709(13)	90(5)
C(5)	2152(15)	453(7)	6695	80(6)
C(6)	2632(16)	338(10)	7868(17)	106(7)
C(7)	1391(15)	56(11)	6629(27)	126(8)
C(8)	2818(9)	1981(7)	−31(13)	45(4)
C(9)	3601(9)	2315(7)	−513(16)	54(5)
C(10)	2068(10)	2176(8)	−749(15)	54(5)
O(3)	2042(7)	2582(5)	−1554(10)	59(4)
O(4)	1419(7)	1825(6)	−365(12)	66(4)
C(11)	666(11)	1919(9)	−1055(21)	74(6)
C(12)	103(12)	1415(12)	−810(28)	126(8)
C(21)	4105(10)	1119(7)	1658(17)	56(5)
C(22)	4762(11)	1401(8)	2238(26)	84(7)
C(23)	5497(14)	1388(11)	1694(37)	135(9)
C(24)	5624(17)	1166(13)	559(39)	151(9)
C(25)	4968(17)	827(10)	−103(24)	114(8)
C(26)	4180(11)	808(9)	484(19)	74(6)
C(31)	2528(8)	534(6)	1814(12)	41(4)
C(32)	1723(11)	621(8)	1432(18)	64(6)
C(33)	1248(15)	107(10)	1068(27)	119(8)
C(34)	1559(15)	−503(11)	992(23)	99(8)
C(35)	2308(14)	−594(8)	1431(20)	85(7)
C(36)	2803(10)	−93(7)	1790(16)	56(5)
C(41)	3239(9)	2935(7)	4773(16)	48(5)
C(42)	3321(11)	3047(9)	6079(17)	64(6)
C(43)	3995(13)	3345(10)	6511(21)	82(7)
C(44)	4598(12)	3544(10)	5789(23)	81(7)
C(45)	4546(12)	3431(10)	4470(19)	73(6)
C(46)	3874(11)	3143(8)	3989(21)	65(6)
C(51)	1532(9)	3149(7)	4024(16)	42(5)
C(52)	1627(10)	3746(7)	4567(19)	59(5)
C(53)	955(13)	4166(9)	4479(22)	85(7)
C(54)	231(12)	3978(10)	3973(20)	76(7)
C(55)	153(11)	3379(10)	3419(19)	75(6)
C(56)	813(10)	2958(8)	3478(21)	73(6)

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

but in the ratio 1:2.5 (cf. 2:1 in the direct reaction shown in Scheme 1). A similar experiment was carried out between N_2CHCO_2(*l*-menthyl) and [PtMe(NCMe)(*S*,*S*-diop)][O_3SCF_3], and the products **12a** and **13a** were obtained in the ratio 1:4 (cf. 2:1 via Scheme 1).

Structure Analysis of [PtCl{*R*-CHClCO$_2$Et}(*S*,*S*-diop)] (2a). Crystal data for **2a**: $C_{36}H_{41}ClO_4P_2Pt$, M_r = 830.2, orthorhombic, space group $P2_12_12$ (No. 18), a = 16.520(5) Å, b = 20.722(6) Å, c = 10.535(4) Å, V = 1930.8(7) Å^3, Z = 4, D_x = 1.53 g cm^{-3}, $\bar{\lambda}$ = 0.710 73 Å, μ(Mo Kα) = 40.9 cm^{-1}, $F(000)$ = 1656, T = 293 K. A single crystal of **2a** (approximate dimensions 0.20 × 0.50 × 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 Siemens R3m/V diffractometer, using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 49 centered reflections in the range $14.0 < 2\theta < 31.0°$. A total of 3808 diffracted intensities, including check reflections, were measured in a unique octant of reciprocal space for $4.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections (1,5,−3; 127; 3,2,−4) remeasured after every 50 ordinary data showed no decay and a variation of ±4% over the period of data collection. Of the 3577 intensity data (other than checks) collected, 3360 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 2802 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 350 azimuthal scan data; maximum and minimum transmission coefficients were 0.727 and 0.292, 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 were refined without positional constraints. All hydrogen atoms were constrained to idealized geometries (C–H = 0.96 Å, H–C–H = 109.5°) with fixed isotropic displacement parameters. A parameter (η) defining the absolute structure, and hence the molecular chirality,[19] was refined to 0.94(4), thereby confirming the handedness of the molecules of **2a** in the crystal studied. Full-matrix least-squares refinement of this model (398 parameters) converged to final residual indices R = 0.047, R_w = 0.054, and S = 1.34.[22] 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 +1.2 to −1.2 e Å^{-3}, the largest of these being close to the platinum atom. Table 4 lists the final atomic positional parameters for the freely refined atoms and Table 2 the selected derived bond lengths and inter-bond angles. Tables in the supplementary material provide the final atomic positional parameters for the non-hydrogen atoms, full lists of the derived bond lengths and interbond angles, the anisotropic displacement parameters, and hydrogen atomic parameters. All calculations were carried out using programs of the SHELXTL-PLUS package.[20] Complex neutral-atom scattering factors were taken from ref 21.

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Supporting Information Available: Text giving additional details of the X-ray study and tables giving additional bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **2a** (7 pages). Ordering information is given on any current masthead page.

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

(20) Sheldrick, G. M. SHELXTL-PLUS Rev. 2.4; University of Göttingen, Göttingen, FRG, 1988.

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

(22) $R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$; $S = [\sum w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$.