Mechanism and Stereochemistry of the Reaction of Dichloroplatinum(II) Complexes with Diazo Compounds. Mono versus Bis Insertion and Competition between Capture of Chloride and Capture of an Internal Nucleophile by Carbenoid Intermediates in the Second Insertion Step

Robert McCrindle* and Alan J. McAlees

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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[(COD)$PtCl_2$] (COD = 1,5-cyclooctadiene) reacts readily with $RCHN_2$ (R = $SiMe_3$, $P(O)(OMe)_2$, CO_2Me) to give the mono-insertion products [(COD)Pt(CHClR)Cl]. With longer reaction times, the bis-insertion products [(COD)$Pt(CHClR)_2$] (*R,R/S,S* isomers predominating) are formed along with other platinum-containing compounds, namely [(COD)Pt(CH_2Cl)(CHCl$SiMe_3$)] (when R = $SiMe_3$), platinaoxaphospholanes (when R = $P(O)(OMe)_2$), or platinalactones (when R = CO_2Me). Mixed bis-insertion products are obtained by reacting the mono-insertion products with a second diazo compound. When the second diazo compound is $N_2CHSiMe_3$, the simple mixed insertion products are accompanied by products of net hydrodesilylation; i.e., they carry a $-CH_2Cl$ ligand rather than $-CHClSiMe_3$. [{(*R,R*)-$Ph_2PCHMeCHMePPh_2$}$PtCl_2$] reacts more slowly with $RCHN_2$ than does the COD complex and gives mono-insertion products in which we suggest the *R* stereochemistry is preferred for the newly created chiral center. A second insertion into the two monoesters with N_2CHCO_2Me proceeds very slowly, giving only minor amounts of simple bis-insertion products, the major products being platinalactones. The mixtures obtained from the (*R*)- and the (*S*)-monoester both contain all four possible isomeric platinalactones, indicating that some inversion of the initial chiral center is taking place. Mechanisms are suggested to account for the nature and stereochemistries of the products formed and the relative rates of some of the reactions. It appears that the results of this investigation can be rationalized by proposing the participation in these reactions of three isomeric types of square-pyramidal carbenoid intermediates, namely (i) axial carbene, which leads to dimerization/oligomerization products, (ii) in-plane carbene with its substituents lying in the main coordination plane, which leads to insertion products, and (iii) in-plane carbene with its substituents above and below the coordination plane, which leads to products of cyclization and hydrodesilylation. This third type of carbene is appropriately aligned to capture an α-Cl from a neighboring CHClR moiety, thus allowing interconversion of carbenes and the possibility of net inversion of configuration at the α-carbon.

Introduction

While there has been considerable interest in reactions of diazo compounds in the presence of transition-metal derivatives,[1] there have been relatively few reports[2-5] of the isolation of simple insertion products formed as follows:

$$M\text{–}X + RR'CN_2 \rightarrow M\text{–}CRR'\text{–}X + N_2$$

Reactions of this type have been reported for M–H,[2,3] M–N,[4] and M–halogen (halogen = Cl, Br, I).[5] Among simple diazo compounds, products of insertion have been isolated from reactions of diazomethane,[6] diazoethane,[5f] 2-phenyldiazoethane,[4a] ethyl diazoacetate,[4b,e,5a,c,e,f] diazoacetonitrile,[7] vinyldiazomethane,[8] 2-diazohexafluoropropane,[2b,c,9] diazoacetone, and diazoacetophenone.[8]

(1) For general reviews, see: (a) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385–5453. (b) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765–1808. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 800–806. (d) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (e) Lappert, M. F.; Poland, J. S. *Adv. Organomet. Chem.* **1970**, *9*, 397–435.

(2) (a) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; pp 63, 68. (b) Cooke, J.; Cullen, W. R.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 1872–1878. (c) Cooke, J.; Cullen, W. R.; Green, M.; Stone, F. G. A. *Chem. Commun.* **1968**, 170–171. (d) Cross, R. J. *Organomet. Chem. Rev.* **1967**, *2*, 97–140.

(3) In at least some cases where both hydride and halide are attached to the metal, insertion into the former bond may be preferred thermodynamically while insertion into the halide bond is preferred kinetically.[6]

(4) (a) Artaud, J.; Gregoire, N.; Leduc, P.; Mansuy, D. *J. Am. Chem. Soc.* **1990**, *112*, 6899–6905. (b) Callot, H. J.; Schaeffer, E. *Nouv. J. Chem.* **1980**, *4*, 311–314. (c) Callot, H. J.; Schaeffer, E. *Nouv. J. Chem.* **1980**, *4*, 307–309. (d) Callot, H. J.; Schaeffer, E. *J. Chem. Soc., Chem. Commun.* **1978**, 937–938. (e) Batten, P.; Hamilton, A. L.; Johnson, A. W.; Mahendran, M.; Ward, D.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1623–1628. (f) Johnson, A. W.; Ward, D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 720–723. (g) Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. L.; Shelton, G.; Elson, C. M.; *J. Chem. Soc., Perkin Trans. 1* **1975**, 2076–2085. (h) Batten, P.; Hamilton, A. L.; Johnson, A. W.; Shelton, G.; Ward, D. *J. Chem. Soc., Chem. Commun.* **1974**, 550–551.

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(6) For leading references see: (a) Reference 2. (b) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; McAlees, A. J.; Sneddon, D. W. *J. Chem. Soc., Dalton Trans.* **1989**, 761–766.

(7) Matsumoto, K.; Odaira, Y.; Tsutsumi, S. *Chem. Commun.* **1968**, 832–833.

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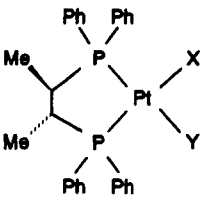
Chart I

$(COD)PtCl_2$	$RCHN_2$		$(COD)Pt(CHRCl)Cl$	
1	2a	R = H	3a	R = H
	2b	R = $SiMe_3$	3b	R = $SiMe_3$
	2c	R = $P(O)(OMe)_2$	3c	R = $P(O)(OMe)_2$
	2d	R = CO_2Me	3d	R = CO_2Me

$(COD)Pt(CHRCl)(CHR'Cl)$

4a	R = R' = H
4b	R = R' = $SiMe_3$ (*R,R/S,S*)
4c	R = R' = $P(O)(OMe)_2$ (*R,R/S,S*)
4d	R = R' = $P(O)(OMe)_2$ (*R,S*)
4e	R = R' = CO_2Me (*R,R/S,S*)
4f	R = R' = CO_2Me (*R,S*)
4g	R = H, R' = $SiMe_3$
4h	R = H, R' = $P(O)(OMe)_2$
4i	R = H, R' = CO_2Me
4j	R = $SiMe_3$, R' = $P(O)(OMe)_2$ (*R,R/S,S*)
4k	R = $SiMe_3$, R' = $P(O)(OMe)_2$ (*R,S*)
4l	R = $SiMe_3$, R' = CO_2Me (*R,R/S,S*)
4m	R = $SiMe_3$, R' = CO_2Me (*R,S*)
4n	R = $P(O)(OMe)_2$, R' = CO_2Me (*R,R/S,S*)
4o	R = $P(O)(OMe)_2$, R' = CO_2Me (*R,S*)



5a	X = Y = Cl
5b	X = $CHClCO_2Me$ (*R*), Y = Cl
5c	X = $CHClCO_2Me$ (*S*), Y = Cl
5d	X = Y = $CHClCO_2Me$ (*R,R*)
5e	X = Y = $CHClCO_2Me$ (*S,S*)
5f	X = Y = $CHClCO_2Me$ (*R,S*)
5g	X = $CHClSiMe_3$, Y = Cl (*R*)
5h	X = $CHClSiMe_3$, Y = Cl (*S*)
5i	X = $CHClP(O)(OMe)_2$, Y = Cl (*R*)
5j	X = $CHClP(O)(OMe)_2$, Y = Cl (*S*)

We have reported the formation of halomethyl derivatives of palladium(II)[6a] and platinum(II)[10] by reaction of diazomethane with a variety of neutral mononuclear complexes of these metals. Ease of insertion was found to depend on the geometry of the starting complex (cis *vs* trans) and the nature of the ancillary ligands. While only mono-insertion products were obtained for the palladium derivatives, platinum complexes gave no insertion, monoinsertion only, or both mono and bis insertion. For example, $[(COD)PtCl_2]$ (**1**; COD = 1,5-cyclooctadiene) reacts with diazomethane (**2a**) to give the mono-insertion product **3a** and the stable bis-insertion product **4a**. Recently, the ruthenium derivative $[(\eta^5\text{-}C_5Me_5)Ru(NO)(CH_2Cl)_2]$[11] was obtained similarly. While numerous mono(halomethyl) derivatives of transition metals have been prepared by oxidative addition of methylene halides,[5d] no bis(halomethyl) compound has been obtained by this route. Indeed, it appears unlikely that the latter approach would be widely applicable. Thus, it seems important to determine if bis insertion is possible for diazo compounds other than diazomethane. As far as we are aware, there are only three examples of products of this type. These were obtained by reaction of $[(Ph_3PPdCl_2)_2]$ with diazoacetonitrile[7] and of $[(PhCN)_2PdCl_2]$ and $[(PhCN)_2PtCl_2]$ with 2-diazohexafluoropropane.[9a,c]

This paper focuses mainly on the outcome of reacting $[(COD)PtCl_2]$ (**1**) and the "chiraphos" complex $[\{(R,R)\text{-}Ph_2PCHMeCHMePPh_2\}PtCl_2]$ (**5a**) with (trimethylsilyl)diazomethane (**2b**), dimethyl (diazomethyl)phosphonate (**2c**), and methyl diazoacetate (**2d**). It was hoped that the results of this study would provide some insight into the steric and electronic requirements of the insertion process, since insertions with diazo compounds of the type $RR'CN_2$ ($R \neq R'$) generate chiral carbon atoms. While both the formation of such insertion products and transition-metal-catalyzed reactions of diazo compounds in general may involve metal carbene intermediates,[1] there has been a dearth of detailed mechanistic proposals in the former area. At least in principle, similar metal carbene species could be regenerated from the initial insertion products and we have suggested that such a process may be involved in the following transformations: cis–trans isomerizations of chloromethyl derivatives,[12] Wagner–Meerwein shifts of chloromethyl, alkyl, and aryl groups from metal to carbon,[13] and the formation of *trans*-$[MePt(PEt_3)_2Cl]$ from *trans*-$[HPt(PEt_3)_2Cl]$ and diazomethane *via trans*-$[HPt(PEt_3)_2(CH_2Cl)]$.[10]

Results

Reactions of $[(COD)PtCl_2]$ (1). Treatment of dichloromethane solutions of **1** with excess diazosilane **2b** at ambient temperature results in rapid (minutes) and clean formation of the monoinsertion product **3b**, which can be isolated as a stable crystalline solid.[14] Even upon prolonged treatment with excess reagent, or on treatment of **3b** with fresh reagent, no clear evidence could be found indicating the presence of bis-insertion product(s). However, when **3b** was exposed to an excess of **2b** (6 molar equiv) in $CDCl_3$ at −17 °C, monitoring by ^1H NMR

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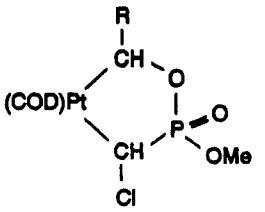
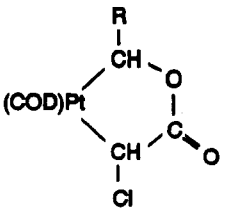
(14) ^1H NMR data for the α-CH's in all complexes isolated, or observed in mixtures, are summarized in Table I and ^{31}P NMR data for P-containing compounds in Table II.

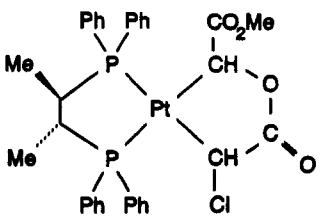
Chart II



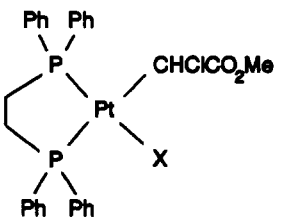
6a R = P(O)(OMe)$_2$ (R, Cl - cis; R, OMe - trans)
6b R = P(O)(OMe)$_2$ (R, Cl - trans; R, OMe - cis)
6c R = H (Cl, OMe - cis)
6d R = H (Cl, OMe - trans)
6e-h R = CO_2Me



8a R = CO_2Me
8b R = H
8c R = $SiMe_3$



	C-2	C-4
9a	*R*	*S*
9b	*R*	*R*
9c	*S*	*R*
9d	*S*	*S*



10a X = Cl
10b X = $CHClCO_2Me$ (*RR/SS*)
10c X = $CHClCO_2Me$ (*RS*)

spectroscopy revealed that the bis-insertion product **4b** was forming very slowly. When the temperature was raised to −5 °C, the rate of this reaction was enhanced, but the production of other products, particularly *trans*-1,2-bis-(trimethylsilyl)ethene, also became apparent. The rate of formation of these products outpaced the insertion process as the solution was warmed to 0 °C. Indeed, when the mixture stood overnight at this temperature, although all of the diazo compound was consumed, only about half of **3b** had reacted. The ^{1}H NMR spectrum at this stage suggested the presence of small amounts of two Pt-containing compounds in addition to a substantial amount (*ca.* 35%) of **4b** (for stereochemical assignment see Discussion). Comparison with the spectrum of material prepared by an alternative route (see below) indicated that one of the minor components was the mixed bis-insertion product [(COD)Pt(CH_2Cl)($CHClSiMe_3$)] (**4g**). A relatively clean sample of the major product, **4b**, was recovered by preparative thin-layer chromatography (TLC) as a solid, which tended to decompose to **1**, even in the refrigerator.

Complex **1** also reacted readily with diazophosphonate **2c** to give the mono-insertion product **3c**. However, in this case, prolonged treatment with excess reagent at ambient temperature gave a mixture of platinum-containing compounds, including both possible products (**4c,d**) of simple bis insertion. Preparative TLC of this mixture gave, in order of increasing polarity, **4c** (60% of recovered material), **4d** (17%), a 4-platina-1,2-oxaphospholane (**6a**, 4%), a second 4-platina-1,2-oxaphospholane (**6b**, 13%), and a compound that appears to be a polynuclear complex containing two distinct types of platinum center (**7**, 6%). The last product was isolated only when the insertion reaction was carried out in concentrated solutions. Bis-insertion products **4c,d** have been crystallized as hydrates. A single crystal of the former, upon X-ray crystallographic examination, proved to contain only molecules of the *R,R* enantiomer,[5a] indicating that **4c** is the *R,R/S,S* pair and that spontaneous resolution has occurred upon crystallization. Thus, **4d** must be the *R,S* isomer. ^{1}H{^{31}P} NMR experiments allowed both the assignment of the α-CH resonances in the ^{1}H NMR spectra of platinaoxaphospholanes **6a,b** and distinction between the signals arising from the endo- and exocyclic phosphorus atoms in their ^{31}P NMR spectra. Consistent with literature reports,[15] the former resonate at lower field than the latter. For both compounds decoupling of the CH next to the ring phosphorus is accompanied by decoupling of a single OMe doublet, while upon decoupling of the CH adjacent to the exocyclic phosphorus the signals for two OMe's suffer collapse. Signals attributable to a third, minor 4-platina-1,2-oxaphospholane (four isomers are possible) were present in the ^{31}P NMR spectrum of the crude reaction product, but this complex was not isolated. Solutions of **4c,d** show no evidence for the formation of **6a,b** during several days. Oligomeric species **7** shows four separate resonances in its ^{31}P NMR spectrum, one of them in the region typical of the 4-platina-1,2-oxaphospholanes (see Table II). Its ^{1}H NMR spectrum shows signals attributable to seven OMe groups, three non-olefinic PtCH's, and apparently only seven olefinic protons.

A mono-insertion product (**3d**) was also rapidly formed when [(COD)$PtCl_2$] was treated with the diazo ester **2d**. Once more, substantial amounts of products resulting from bis insertion, namely **4e,f** and the platinalactone **8a**, could be recovered when this reaction was allowed to proceed for several days. Indeed, when the reaction was carried

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Table I. ^{1}H NMR Data for the α-CH's in the Insertion Products

compd	δ_H	J_{Pt-H}, Hz	J_{P-H}, Hz	compd	δ_H	J_{Pt-H}, Hz	J_{P-H}, Hz
3a	3.97	74		**6a**	5.23	105	4.0, 1.9
3b	4.46	94			4.90	98	10.9
3c	4.72	106	9.2	**6b**	5.37	103	2.4
3d	4.91	110			4.90	98	11.2
4a	3.84	60		**6c**	4.72	111	10.9
4b	3.63	75			4.98	74	1.6, 9.0[a]
4c	4.29	86	11.3		4.58	77	23.7, 9.0[a]
4d	4.24	92	10.5	**6d**	4.64	103	10.0
4e	4.92	100			4.77	78	3.8, 9.2[a]
4f	4.79	105			4.61	75	22.4, 9.2[a]
4g	3.90	84		**6e**	4.99	*b*	11.8
	3.91	62	9.8[a]		5.43	*b*	3.2
	3.50	54	9.8[a]	**7**	4.39	90	10.6
4h	4.05	94	11.2		4.85	91	5.5
	4.01	58	9.2[a]		5.45	*b*	5.2, 2.8
	3.75	62	9.2[a]	**8a**	5.98	128	
4i	4.38	106			5.52	128	
	4.12	60	9.8[a]	**8b**	5.83	137	
	4.00	63	9.8[a]		4.98	96	9.8[a]
4j	3.58	83	12.8		4.84	53	9.8[a]
	4.04	75		**8c**	5.91	136	
4k	3.94	94	9.9		5.34	114	
	4.09	90		**9a**	5.64	94	9.0, <1
4l	4.47[c]	79			5.05	93	7.5, 7.1
	4.12	96		**9b**	5.42	86	8.9, 3.9
4m	4.28[c]	88			4.08	51	7.2, 4.4
	4.19	97		**9c**	5.79	90	9.9, 1.4
4n	4.59	88	10.7		5.38	98	8.7, 6.1
	4.70	97		**9d**	5.26	95	8.9, 6.0
4o	4.37	91	10.7		4.29	27	6.7, 3.2
	4.62	103		**10a**	4.46	75	9.7, 6.8
5b	4.35	86	9.2, 5.3	**10b**	4.89	100	8.8[d]
5c	4.35	78	9.4, 6.4	**10c**	4.85	98	8.6[d]
5d	4.74	100	7.5[d]				
5e	4.83	103	6.3[d]				
5f	4.81	104	8.7, 5.7				
	4.63	95	12.1, 8.1				
5g	3.29	30	10.7, 7.3				
5i	4.07	73	10.1, 8.0, 5.1				

[a] J_{H-H}. [b] Not observed. [c] Value for C*H*ClSiMe$_3$. [d] Apparent triplet.

out in $CDCl_3$ and the progress monitored by NMR spectroscopy, mono insertion was complete within 3 h and signals for **4e,f** were already observable in a ratio of 5:4, respectively. However, it was difficult to push the reaction to completion even upon addition of further quantities of the diazo ester, which tended to suffer conversion to other products such as dimethyl maleate and fumarate at a rate which is competitive with that of the second insertion step. Recrystallization of substantially pure samples of the bis-insertion products **4e,f** failed to free them from traces of **3d**, which is present in the reaction mixture and also appears to form from both during TLC. Like the bis phosphonates, these bis esters showed no tendency to cyclize either during TLC or upon standing in solution. Ligand displacement from both with (*R,R*)-chiraphos (see below) established that **4e** is the *R,R*/*S,S* isomer and **4f** the meso form. We have obtained **8a** only as a gum, even after repetitive preparative TLC, possibly because it contains a small amount of a stereoisomer as evidenced in particular by the presence of two signals (*ca.* 10:1 ratio) ascribable to OMe groups in its ^{1}H NMR spectrum and the outcome of treating it with (*R,R*)-chiraphos (see below).

Reactions of Monoinsertion Products 3a–d. Formation of unsymmetrical bis-insertion products, by reaction of **3a–d** with the appropriate diazo derivatives, was investigated in the hope of disclosing some aspects of the steric and electronic features that are important in the second insertion step.

Table II. ^{31}P NMR Data for P-Containing Insertion Products

compd	δ_P	J_{Pt-P}, Hz	J_{P-P}, Hz	compd	δ_P	J_{Pt-P}, Hz	J_{P-P}, Hz
3c	27.6	13		**6a**	44.0	152	42
4c	29.2	32			27.7[a]	44	42
4d	30.3			**6b**	37.8	134	45
4h	30.6	12			28.6[a]	48	45
4j	29.9	15		**6c**	42.7	156	
4k	31.2			**6d**	46.8	173	
4n	29.8	34		**6e**	37.3	142	
4o	30.1			**6f**	43.4	161	
5b	41.1	3983	16	**6g**	43.8	162	
	39.9	2023	16	**6h**	44.3	146	
5c	41.1	3959	16	**7**	43.6	118	39
	40.5	2040	16		32.5	19	
5d	43.0	2268			30.7	27	
5e	40.9	2255			30.2	43	39
5f	44.0	2203	13	**9a**	45.7	2115	13
	41.4	2326	13		45.4	2360	13
5g	41.7	1773	12	**9b**	45.9	2313	12
	41.1	4086	12		40.8	2039	12
5h	43.0	1738	15	**9c**	50.4	2368	9
	42.4	4264	15		44.5	2179	9
5i	41.4	3969	16	**9d**	46.8	2016	13
	40.5	2031	16, 3		44.4	2314	13
	32.2	32	3	**10a**	40.8	4018	5
5j	41.6	3939	16		39.8	2095	5
	40.8	2012	16, 3	**10b**	43.3	2287	
	32.7	40	3	**10c**	43.6	2287	

[a] Exo.

Earlier work[10] had shown that [(COD)Pt(CH_2Cl)Cl] (**3a**) is converted smoothly into [(COD)Pt($CH_2Cl)_2$] when exposed to diazomethane. We have now found that **3b–d** also suffer a rapid second insertion with this reagent, giving **4g–i**, respectively.

Phosphonate complex **4h** and ester complex **4i** are reasonably stable in solution, but upon removal of solvent or exposure to preparative TLC, both undergo ring closure. Thus, when allowed to stand as a gum, **4i** formed platinalactone **8b** over several days while **4h** gave a mixture of a major 4-platina-1,2-oxaphospholane, **6c**, and diastereomer **6d** over a period of several weeks. In each decomposition, an essentially stoichiometric amount of a product of Pt–C bond cleavage was also formed; **3a** from **4i** and **3c** from **4h**. It is noteworthy that in the case of **4h** it is the Pt–CH_2Cl bond that cleaves while with **4i** this bond survives.

(Trimethylsilyl)diazomethane (**2b**) also reacted rapidly with **3a,c,d** to give bis-insertion products. The product (**4g**) derived from **3a** was, as anticipated, identical with that formed earlier from the monosilyl derivative **3b** and diazomethane. A ^{31}P NMR spectrum of the crude mixture from the reaction of monophosphonate **3c** with **2b** contained resonances attributable to three predominant species, a major (**4j**) and a minor (**4k**) bis-insertion product of the type expected and **4h**, originating from hydrodesilylation. Also present were very minor signals arising from platinaoxaphospholanes **6c,d**, formation of which requires both hydrodesilylation and cyclization steps. Mixed insertion products **4j,k** were recovered by preparative-scale TLC. Reaction of the monoester **3d** with **2b** gave a mixture whose ^{1}H NMR spectrum indicated the presence of the mixed bis-insertion products **4l,m** and the hydrodesilylated product **4i** (*ca.* 3:2:2). Attempted purification by preparative TLC resulted in partial conversion of the initial products into platinalactones **8b,c** and the three products of Pt–C bond cleavage **3a,b,d**. Higher proportions of these transformation products were ob-

tained when the reaction mixture was left on the plates for several hours before development. Further, **4l,m**, when left standing in mixtures as gums, tend to cyclize, as does **4i** (see above), and hydrodesilylate to give **8b,c** along with cleavage products **3a,b**.

[(COD)Pt(CH_2Cl)Cl] reacts substantially more slowly with the diazophosphonate **2c** than with either diazomethane or even the silyl derivative **2b**, requiring several hours to attain completion. The reaction is very clean, giving apparently a single Pt-containing product, **4h**, with little or no 4-platina-1,2-oxaphospholane or concomitant oligomerization of **2c**. The diazophosphonate reacts even more sluggishly with monosilyl complex **3b**. In this case, although reaction was still incomplete after 3 weeks at room temperature, two isomeric bis-insertion products were isolated from the resulting mixture, a major component, **4j**, and a more polar, minor component, **4k**. The rate of reaction of **2c** with monoester complex **3d** is also relatively slow, reaching completion only after 4 days. Again only two products were detected in the reaction mixture by ^1H and ^{31}P NMR spectroscopy, a major, **4n**, and a minor, **4o**, isomer. Resonances ascribable to platinalactones or platinaoxaphospholanes were not observed.

A study of the reactions of the diazo ester **2d** with **3a–c** revealed a scenario very similar to that for the analogous reactions outlined above for **2c**. The diazo ester may be slightly less reactive than the diazophosphonate, but the former is much more susceptible to oligomerization in the presence of the insertion products, and the resulting loss of reagent makes comparison of rates difficult. The mono(chloromethyl) complex **3a** is largely consumed within 18 h, giving the mixed bis-insertion product **4i** as the only Pt-containing species detectable by ^1H NMR spectroscopy. In contrast, the reaction of **2d** with monophosphonate complex **3c** is only *ca.* 85% complete in 6 days. A ^{31}P NMR spectrum of the crude product contained resonances arising from the same two isomers (**4n,o**) produced in the reaction of **2c** with **3d**, although now in very similar amounts, as well as resonances attributable to minor amounts of four isomeric 4-platina-1,2-oxaphospholanes, **6e–h**. Reaction of monosilyl complex **3b** with **2d** gave no detectable quantities (^1H NMR) of the mixed insertion products (**4l,m**), although **2d** was consumed in less than 1 week, giving mainly products of oligomerization. However, the ^1H NMR spectrum of the product at this stage showed peaks attributable to the desilylated bis-insertion product **4i** and unreacted substrate **3b**.

Reaction of Mono- (3d) and Bis(ester) (4e,f) Complexes with 1,2-Bis(diphenylphosphino)ethane. As mentioned above, our assignment of configurations to **4e,f** rests on the outcome of displacing 1,5-cyclooctadiene from these complexes with (*R,R*)-chiraphos. Before attempting this reaction, we investigated the conditions required using the less expensive ligand 1,2-bis(diphenylphosphino)ethane (DPPE). With the intention of monitoring these reactions using ^1H NMR spectroscopy, stoichiometric quantities of the reagents were dissolved in $CDCl_3$. The samples of **4e,f** used contained detectable amounts of the corresponding monoester, which, as mentioned above, tends to be a ubiquitous impurity. Under these conditions, both diesters reacted relatively slowly, requiring several hours to reach completion. The monoester, on the other hand, was very rapidly consumed (see below). The products, **10b,c** from the diesters were purified by preparative TLC and characterized by ^1H and ^{31}P NMR spectroscopy.

The monoester **3d** in these reaction mixtures is converted cleanly into the relatively insoluble complex [$(DPPE)_2Pt$]Cl_2. Formation of ionic species upon reaction of complexes of the type [$L_2Pt(R)Cl$] (R = organic fragment) with phosphines in relatively polar solvents, such as chloroform, is well-known.[16] Often a mixture of products, some of which have lost the R group, results. Generally, the fate of the lost organic moiety has not been discussed. The observation that **3d** reacts rapidly and cleanly with DPPE induced us to repeat this reaction on a pure sample of the complex.

When an equimolar amount of DPPE was dissolved in a solution of **3d** in $CDCl_3$, the solution darkened and colorless [$(DPPE)_2Pt$]Cl_2 started precipitating immediately. A ^1H NMR spectrum run after 30 min revealed that all the phosphine, but only about half of the **3d**, had reacted.[17] This spectrum also showed weak signals attributable to the expected product of ligand substitution, **10a**. Essentially total conversion into [$(DPPE)_2Pt$]Cl_2 was achieved by adding an addition 1 molar equiv of DPPE. A ^1H NMR spectrum of the filtrate obtained by removal of the [$(DPPE)_2Pt$]Cl_2 indicated that the product formed from the $CHClCO_2Me$ fragment gives rise to what appeared to be a curiously shaped multiplet at *ca.* 4.05 ppm. A closer study of this signal revealed that it is made up of two resonances, one attributable to methyl chloroacetate and the other to $ClDHCCO_2Me$ in an approximate ratio of 1:8. As anticipated, when **3d** was exposed to 1 molar equiv of DPPE in benzene, the substitution product **10a** was formed rapidly and cleanly. This product, upon dissolution in $CDCl_3$ and reaction with a further 1 molar equiv of DPPE, was smoothly converted into [$(DPPE)_2Pt$]Cl_2. A ^1H NMR spectrum of the supernatant solution again showed the presence of methyl chloroacetate and its monodeuterio derivative and, in addition, a pronounced enhancement in the intensity of the signal due to residual $CHCl_3$ in the solvent. A deuterium NMR spectrum of this solution revealed the absence of $ClCD_2CO_2Me$ but showed the presence of a substantial amount of D_2CCl_2 ($ClDHCCO_2Me$:D_2CCl_2 *ca.* 6:1).[18]

Reactions involving Complexes of (*R,R*)-chiraphos. On the basis of our experience with DPPE, we attempted the replacement of the COD ligand in the diester complexes **4e,f** by dissolving stoichiometric quantities of the complex and the chiral ligand in a minimum amount of $CDCl_3$ under nitrogen. After 3 days, ^1H and ^{31}P NMR spectra were run on the reaction mixtures. These showed that although neither reaction was complete, **4e** gave two simple replacement products, **5d,e**, while **4f** gave only one, **5f**, thus demonstrating that **4e** is the *R,R/S,S* pair and **4f** the *R,S* diastereomer. The products were recovered by preparative TLC. However, in both cases, the yields were low, the major product, on the basis of ^{31}P NMR spectroscopy only, being [{(*R,R*)-chiraphos}$_2$Pt]Cl_2.

Since only small amounts of **5d–f** were obtained above and all three compounds are well resolved on TLC, we

(16) You, Y.-J.; Chen, J.-T.; Cheng, M.-C.; Wang, W. *Inorg. Chem.* **1991**, *30*, 3621–3625.

(17) Surprisingly, the reaction of [(COD)Pt($CHClCO_2Et$)Cl] with DPPE in $CDCl_3$ is reported to give the simple replacement product [(DPPE)Pt($CHClCO_2Et$)Cl].[5c]

(18) These results may indicate that both ionic and radical intermediates are involved in the fragmentation process with ubiquitous water as a likely source of the protium. *Cf.*: McCrindle, R.; Ferguson, G.; McAlees, A. J.; Parvez, M.; Roberts, P. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1699–1708.

attempted to prepare them by reacting the relatively insoluble [{(*R,R*)-chiraphos}$PtCl_2$] (**5a**) with the diazo ester **2d** in dichloromethane. After 3 days at 4 °C the solvent was evaporated. A ^{31}P NMR spectrum of the resulting mixture in $CDCl_3$ revealed the presence of three predominant constituents, substrate (**5a**) and both monoesters, **5b,c**, in an approximate ratio of 5:3:2. When this solution was treated with a further amount of **2d** and then left at ambient temperature for 1 week, the following species were detected: major amounts of one monoester (**5b**) and a product to which we ascribe the platinalactone structure **9a** smaller amounts of the other monoester (**5c**) and three further platinalactones (**9b–d**), isomeric with **9a**, and traces of the three diesters (**5d–f**). Exposure to more **2d** for an additional 1 week led to the loss of the monoesters and a concomitant increase in the concentrations of the other constituents. We have not found it possible to separate the isomeric lactones by preparative TLC, but our ^{13}C, ^{31}P, and ^{1}H NMR data on partially resolved mixtures strongly support the gross structures assigned.

A puzzling feature of this insertion reaction is the observation that one platinalactone, **9a**, greatly predominates in the final mixture, although early in the reaction relatively comparable amounts of monoesters **5b,c** are formed. This appeared to imply that both monoesters can give rise to **9a**. That such is indeed the case was verified by preparing samples of **5b,c** and exposing them, separately, to **2d** in both C_6D_6/dichloromethane (1:1) and $CDCl_3$. Monitoring all four experiments by ^{31}P NMR spectroscopy revealed that insertion occurs more rapidly for both substrates in the latter solvent and that **5c** reacts more quickly than **5b** in either solvent. In all cases, at least minor amounts of all four platinalactones were detected and **9a** was the major product. However, in relative terms, more **9a,d** formed from **5c** while **5b** generated more **9b,c**. There was no apparent change in the ratios of the platinalactones formed over the course of the reaction in all four experiments. The same four platinalactones were generated by reaction of the COD-containing analogue **8a** (10:1 isomer mixture) with (*R,R*)-chiraphos. In the resulting mixture of **9a–d**, the ratio of both **9a**:**9c** (major) and **9b**:**9d** (minor) was 1:1. Attempted separation by preparative TLC of this mixture produced a different mixture in which **9c** had been largely replaced by **9b**.

As indicated above, preparation of monoinsertion products **5b,c** from dichloride **5a** by reaction with methyl diazoacetate is inconvenient since insertion is very slow and platinalactone formation intervenes before consumption of **5a** is complete. Thus, these complexes were prepared by reaction of the COD complex **3d** with (*R,R*)-chiraphos in benzene and the resulting mixture of diastereomeric complexes was separated by preparative TLC.

We have also briefly investigated the reaction of **5a** with both the diazosilane (**2b**) and the diazophosphonate (**2c**) in anticipation of obtaining better diastereoselectivity than with the less sterically demanding diazo ester. At ambient temperature both **2b** and **2c** gave the two possible monoinsertion products (**5g** (major) and **5h**; **5i** (major) and **5j**, respectively) in a *ca.* 5:1 ratio in both cases. At 4 °C the ratios changed to *ca.* 20:1 for the former and 8:1 for the latter.

Discussion

Stereochemistries of Platinaoxaphospholanes 6a–d. The stereochemical assignments for platinaoxaphospholanes **6c,d** are based on a comparison of the chemical shifts and coupling constants of the three protons attached to the platina-1,2-oxaphospholane ring with those for the analogous protons in a number of variously substituted 1,2-oxaphospholanes.[19] The magnitudes of the $^{3}J_{P-H}$ coupling constants indicate that in both complexes one of the geminal protons is pseudoaxial (small coupling) and the other pseudoequatorial (large coupling). This may indicate that the compounds prefer an envelope-type conformation with either the P–O–C or the C–Pt–C moiety serving as the flap (see Figure 1). The downfield shifts of the resonances arising from the pseudo-axial geminal proton and CHCl in **6c**, relative to those for **6d**, suggest that both are syn to the phosphonyl (P=O) bond in the former. The ^{1}H NMR data reported in Table I for **6a,b** suggest that these complexes exist in a conformation similar to that of **6c,d**, with the exocyclic phosphonate groups in the former pair taking the place of the pseudoequatorial hydrogen atoms in the latter. The configurations deduced for **6a,b** are those expected on mechanistic grounds (see below).

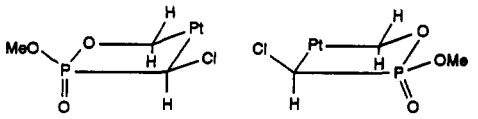


Figure 1. Possible conformations of the platinaoxaphospholane fragment for **6c**.

Stereochemistries of Mixed Bis-Insertion Products with Two Chiral Centers. The stereochemistries shown for the mixed bis-insertion products **4j–o** were assigned on the basis of the following observations. As with the symmetrical bis-insertion products (**4c/4d** and **4e/4f**) whose stereochemistries have been established, the less polar isomer on TLC is the major product and also shows the smaller values for $^{2}J_{Pt-H}$ couplings (see Table I). In addition, major isomers **4c,j,n** show observable $^{2}J_{Pt-P}$ couplings while the corresponding minor isomers, **4d,k,o**, do not. It is not surprising that the *R,R*/*S,S* pair is less polar than the *R,S* isomer. For example, in (*R,R*/*S,S*)-bisphosphonate complex **4c** the substituents on the chiral carbons can adopt conformations in which similar substituents are related by a 2-fold symmetry axis (as in the crystal structure[5a]), thereby minimizing the net polarity of the molecule, while a comparable disposition of substituents is not possible for the *R,S* isomer **4d**. At this stage we have no satisfactory explanation for the origin of the observed trend in the coupling constants.

Stereochemistries of the Platinalactones 8a and 9a–d. Deduction of the stereochemistries shown for these derivatives started from the observations that reaction of diazo ester **2d** with either of the chiraphos monoester complexes **5b,c** gives all four possible platinalactone products **9a–d** and that **9a** is the predominant product in both cases. The former observation indicates that some inversion at the original α-carbon atom of **5b** and **5c** is taking place during the course of the reaction, while the second observation suggests that **9a** is the most stable product of the group. In relative terms, more **9a,d** formed from **5c**, while **5b** generated more **9b,c**, implying that the configuration at the CCl carbon in the starting monoesters **5b,c** is carried over into the pairs of products **9b**/**9c** and **9a**/**9d**, respectively. A study of molecular models, if one

(19) Pondaven-Raphalen, A.; Sturtz, G. *Phosphorus Sulfur Relat. Elem.* **1988**, *36*, 39–52.

bears in mind the expected conformation of the (*R,R*)-chiraphos moiety (see mechanistic discussion below), suggests that the thermodynamically most stable platinalactone should have *S* and *R* configurations at the CCl and HCO carbons, respectively, while the least stable should have the *R* and *S* configurations at these centers. This argument led us to make the tentative assignments of configuration shown for **9a**, the preferred product, and consequently for **9d**, if these have the same configuration at the CCl carbon, as suggested above.

Assignment of configuration to **9b,c** is based on the outcome of the reaction of platinalactone **8a** (10:1 isomer mixture) with (*R,R*)-chiraphos, which generated a mixture of **9a–d**, in which the ratio of both **9a:9c** (major) and **9b:9b** (minor) was 1:1. Thus, if the substituents on the platinalactone ring of **9a** are trans, then this must also hold for **9c**. These tentative configurational assignments gain some support from the following observations. (i) A study of models also suggests that while the monoester with the *R* configuration at the α-carbon should be the major product of initial insertion into **5a** (see discussion of mechanism below) the monoester with the *S* configuration at the α-carbon should be less hindered to attack by the diazo ester. We do find that the faster reacting ester, **5c**, is the one that gives more **9a,d**. (ii) Attempted separation by preparative TLC of the mixture of **9a–d** prepared from **8a** produced a different mixture in which **9c** had been largely replaced by **9b**.[20] Interestingly, **9c** was predicted (see above) to be the least stable isomer.

Stereochemistries of Chiraphos Bis(ester) Complexes 5d–f. From the reactions of the monoester chiraphos complexes **5b,c** with diazo ester **2d**, only small amounts of the corresponding diesters were obtained, **5e** and a trace of **5f** from **5c**, and **5d,f** from **5b**. However, if our assignment of configurations to **5b,c** is correct, this demonstrates that **5d** is the *R,R,R,R* isomer and **5e** the *R,R,S,S* isomer. These diesters appear to be stable under the reaction conditions employed and are therefore unlikely to be intermediates in the formation of the platinalactones.

Insertion Mechanism. We have previously invoked[6b,10,12,13,21] the intermediacy of carbenoid species in a number of transformations investigated during the course of earlier work in this area and have speculated that five-coordinate neutral and/or square-planar cationic species may be involved. As indicated in a recent publication,[22] there has been little interest in the subject of cationic carbene complexes of platinum despite the considerable effort devoted to the study of carbenoid derivatives of earlier transition metals. In particular, for reactions with diazo derivatives, there is a paucity of information upon which a detailed mechanistic picture of both the formation of the initial carbenoid intermediate and the subsequent insertion step can be based.

In proposing appropriate mechanisms, we have to account for the following: (i) the stereoselectivity of the first insertion step in the reactions of the diazo compounds **2b–d** with the chiraphos complex **5a**, (ii) the stereoselectivity of the reaction of the chiraphos monoester complexes

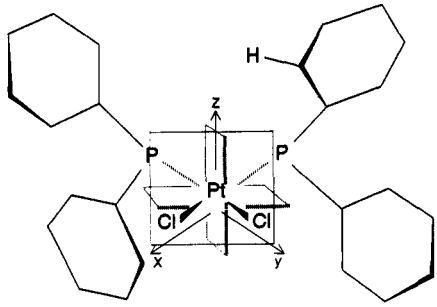


Figure 2. Expected orientation of the phenyl groups in **5a** with a set of reference planes and axes. The ligand backbone has been omitted for clarity.

5b,c with diazo ester **2d** and in the formation of diastereomeric products from [(COD)$PtCl_2$], (iii) the formation of cyclic products, (iv) the relative rates of reaction of the different diazo compounds, and (v) the formation of olefinic and other byproducts. We focus first on the reactions of **5a**, the structure of which is depicted in Figure 2 along with a set of reference planes and axes: the Pt–Cl bonds lie along the *x* and *y* axes, and the vertical planes bisect these two axes. The planes divide the coordination sphere into a set of octants. The phenyl groups of the (*R,R*)-chiraphos ligand, which exert steric control of access to the axial sites of the Pt, lie in the rear four octants and can be divided into two symmetry-related pairs. The preferred conformation of the complex is expected[23] to be one in which both methyl groups in the five-membered chelate ring are pseudoequatorial. This constraint induces the pair of phenyls in the upper right and lower left octants to become oriented in such a way that an ortho hydrogen of each lies close to the adjacent empty axial coordination site. These phenyl groups effectively inhibit access into the octants that they occupy. The other pair lie closer to the coordination plane and are much less effective in blocking approach to the metal center. For convenience in the subsequent discussion we use the terms "axial" and "equatorial" to describe groups or atoms lying approximately parallel to the *z* axis or the *xy* plane, respectively.

Monoinsertion Reactions of [{(*R,R*)-chiraphos}-$PtCl_2$] (5a). Starting from the generally accepted assumption[24] that reaction of transition-metal derivatives with diazo compounds usually proceeds *via* unstable diazo complexes that lose nitrogen to form carbene complexes, we have considered two possible ways in which a carbenoid intermediate might be formed from **5a** *via* initial formation of labile diazo adducts. In the first of these (Scheme I), the diazo compound is bonded *via* the carbon atom with subsequent carbene formation resulting from direct nitrogen loss (path a). In the second, the diazo compound is bonded *via* the terminal nitrogen atom with carbene formation proceeding *via* a formal 1,3-dipolar cycloaddition followed by nitrogen extrusion (path b).[25] Since the two axial sites in **5a** are equivalent, attack at either of them by $RCHN_2$ will lead to the same stereochemical outcome.

In path a, with attack from the upper face, steric interactions in the initial carbon-bonded intermediate (A) are minimized if the hydrogen atom is directed toward

(20) If our assignment of configurations to **9a–d** is correct, this interconversion requires epimerization at the HCO carbon in **9c**. This might proceed *via* a carbenoid intermediate generated by acid-catalyzed heterolysis of the C–O bond on the TLC plates.

(21) McCrindle, R.; Arsenault, G. J.; Gupta, A.; Hampden-Smith, M. J.; Rice, R. E.; McAlees, A. J. *J. Chem. Soc., Dalton Trans.* **1991**, 949–954.

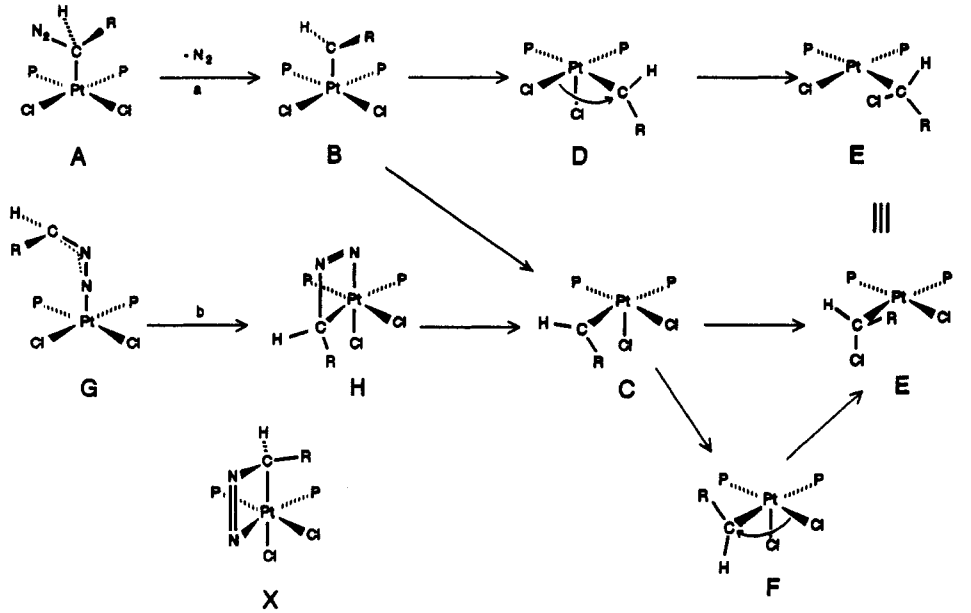
(22) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766–1769.

(23) (a) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905–4916. (b) Brunner, H.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta* **1985**, *96*, 67–75.

(24) Reference 1c, p 198.

(25) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, p 158.

Scheme I



the space between the axial and equatorial phenyl groups, with the N_2 substituent lying essentially parallel to the equatorial phenyl and the bulkier R substituent pointing out into the front, upper right, octant. In order to accommodate this new axial substituent, hindrance by the ortho H that partially blocks this site (see Figure 2) is presumably attenuated by conformational adjustments in the chiraphos moiety. Loss of N_2 from A should give the carbenoid intermediate B, in which the H–C–R plane coincides with the *yz* plane as defined in Figure 2, i.e. with the carbenoid p orbital suitably aligned for overlap with the filled Pt d_{xz} orbital.[26] If the reaction then proceeds, as we have suggested previously,[10] like a nucleophilic substitution process, B would be converted (*via* a trigonal-bipyramidal species) into either C or D, in both of which the carbene lies in the coordination plane with its p orbital suitably aligned for overlap with either the filled Pt d_{xy} orbital (D) or d_{xz} orbital (C). These species could be regarded as five-coordinate neutral carbenes, as depicted, or as cationic carbenes with a closely associated chloride counterion in the axial site.[27] Formation of the final product E from C would simply involve migration of the axial Cl onto the carbene carbon, while conversion of D into E would require migration of the in-plane Cl onto the carbene carbon and transfer of the axial Cl into the vacated site. Although a sequence very similar to this latter process has been proposed for the well-studied insertion of CO into Pt–C bonds,[28] we prefer the route *via* C on stereoelectronic grounds.[29]

In alternative pathway b, the octahedral intermediate H could be formed either stepwise *via* N-coordinated species G (or indeed, C-coordinated species A) or directly by a 1,3-dipolar cycloaddition.[30] Formation of H, as opposed to possible stereoisomers, is preferred because it does not involve steric interaction between the R group of the diazo compound and phenyl groups, and the diazo H atom lies close to an equatorial phenyl rather than a more sterically demanding axial one. Loss of N_2 from H would then give the square-pyramidal carbene C. Either pathway, as drawn, predicts that the preferred configuration at the α-carbon in the monoinsertion products from reaction of **5a** with $RCHN_2$ is *R* and that this preference should increase with increasing bulk of the substituent R. Formation of the *S* isomer could conceivably involve intermediates analogous to B (or H) in which the H and R substituents are interchanged. Although we have not established the configuration at the α-carbon atom in any of the monoinsertion products (**5b,c,g–j**), other workers have found[5c] that [{(*R,R*)-DIOP}$PtCl_2$], in which the phosphine ligand phenyl substituents have a disposition similar to that in **5a**, gives mainly the monoinsertion product with the *R* configuration upon reaction with ethyl diazoacetate.

Reactions of Monoinsertion Products 5b,c with Diazo Ester 2d and Formation of Cyclic Products. The assignment of *R* and *S* configurations to the α-carbons in **5b,c**, respectively, is supported by their behavior upon further reaction with **2d**. Because of the steric requirements of the chiraphos ligand as pictured in Figure 2, one would expect the preferred conformation of the CHClR fragment of a monoinsertion product to be one in which the bulkiest substituent, R, occupies an axial position in either the lower right or the upper left front octant. Thus, for example, the preferred conformation of **5b** should be

(26) A carbenoid intermediate analogous to B but having the H–C–R plane coincident with the *xz* plane would be destabilized relative to B by steric interaction between the carbene H atom and the axial phenyl group.

(27) *Cf.*, for example, the square–planar/square-pyramidal complexes described in: Salem, G.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 581–586.

(28) (a) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937–1948. (b) Anderson, G. K.; Lumetta, G. J. *Organometallics* **1985**, *4*, 1542–1545. (c) Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67–74.

(29) A migration of this type might explain why reaction of diazomethane with [(COD)Pt(CH_3)Cl] gives [(COD)Pt(CH_3)(CH_2Cl)] (the product of Cl migration) rather than [(COD)Pt(CH_2CH_3)Cl] (the product of methyl migration), although the former product is converted into the latter upon dissolution in a polar solvent.[13] This latter rearrangement may proceed via a carbene of type D. Note also that if, in the formation of E from C, migration can only occur within the main coordination plane, prior rotation of the carbene moiety would have to take place so that the C p orbital becomes aligned with the filled Pt d_{xy} orbital. In the preferred orientation (F), the bulky group R escapes from a steric interaction with an axial phenyl group which it would suffer if it were interchanged with the H. In this orientation, migration of the in-plane Cl would again generate E.

(30) Consideration of pathways involving the possible alternative intermediate X, formed by 1,3-dipolar cycloaddition, leads to the same stereochemical conclusions.

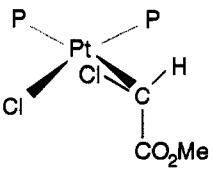


Figure 3. Illustration of the preferred conformation of the $PtCHClCO_2Me$ fragment of **5b** (phosphine ligand substituents as in Figure 2).

that shown in Figure 3. Indeed, this is the conformation found for the analogous complex [{(*R*,*R*)-DIOP}Pt{(*R*)-$CHClCO_2Et$}Cl] by X-ray crystallography.[5c] The preferred conformation of **5c** should be similar but with the α-H and α-Cl interchanged, thus placing the latter in a more hindered site between two phenyl groups. For both complexes in their preferred conformations, approach of **2d** to one axial site is blocked by the axially disposed ester group while approach to the other axial site involves encounter of the R group in **2d** with the H atom in the case of **5c** and Cl in the case of **5b**. This rationalizes the observed greater rate of reaction of **5c**. If reaction of **5c** proceeds through intermediates analogous to B or H in Scheme I, the species I (Scheme II) would be formed. Capture of the displaced chloride would give the bis-insertion product **5f**. This may be relatively unfavorable because severe steric congestion prevents the chloride from occupying the axial coordination site (separated ion-pair?). Note that the reactions of **5b,c** occur significantly more rapidly in the more polar solvent chloroform. Formation of the platinalactone **9a** from I requires at least partial counterclockwise rotation of the carbenoid fragment toward the vertical orientation with respect to the coordination plane (see J), nucleophilic attack by the carbonyl group of the neighboring, axially disposed ester function on the carbenoid carbon, and displacement of the ester methyl group by a nucleophile (ubiquitous water,[31] chloride) present in the reaction solution. A similar sequence may lead to the isomeric platinalactone **9d** if rotation of the carbenoid fragment of I occurs in the sterically less favorable clockwise sense (see K; carbenoid ester interacting with both an axial phenyl and the other ester group). An alternative, and perhaps preferable, route to **9d** would involve the carbenoid species analogous to I but with the H atom and ester group interchanged. Chloride capture by such an intermediate would lead to the bis-insertion product **5e**. In the case of this intermediate, rotation of the carbene moiety in either direction appears to be more difficult than for I, and indeed **5e** is the major product of chloride capture. However, although perhaps more arduous than for I, counterclockwise rotation should again be preferred, leading in this instance to **9d** *via* K. The formation of small amounts of platinalactones **9b,c**, along with **9a,d**, initially came as a surprise because this "leakage" through to the former pair requires an apparent inversion of stereochemistry at the carbon bearing the Cl substituent. Since a pathway involving the diesters **5e,f** as intermediates can be excluded (see above), it seems clear that chlorine migration from α-carbon to the carbene carbon is responsible. Such a migration is possible only if intermediate J adopts the relatively unfavorable conformation depicted in L, thus explaining the relatively small amount of leakage observed in this reaction. α-Cl migration from the *S* center in L would then give M, in which the newly generated chiral center has the *R* configuration. Conformational adjustments and ring closure would finally lead to **9b,c**.

5b not only reacts more sluggishly with diazo ester **2d** than does **5c**, it also gives a greater proportion of diesters and leakage products. The preferred avenue of reaction of **5b** should lead initially to intermediate N, which would generate bis-insertion product **5d** by chloride capture. One might anticipate that, relative to I, N would give more diester since rotation of the carbene fragment, which leads to ring closure, should be more difficult in this case. Of the two possible directions of rotation, clockwise seems easier since counterclockwise rotation would be hindered by interaction between the carbene ester and the α-Cl. In the resulting intermediate O, clockwise rotation of the other carbon ligand would allow the ester group to interact with the carbene, leading to platinalactone **9c**. However, this latter rotation requires the α-Cl to be thrust up against the axial phenyl group. An alternative fate for O thus seems preferable. In this intermediate, the α-Cl appears to be ideally oriented to migrate to the carbene carbon to give P, which would, in turn, lead to the most stable of the platinalactones, **9a**, after conformational adjustment. If, initially, the less favorable carbenoid intermediate Q is produced, this can either capture Cl to give diester **5f** or suffer preferential clockwise rotation of the carbenoid fragment to give R, which could then close to **9b**. α-Cl migration in R would simply regenerate R.

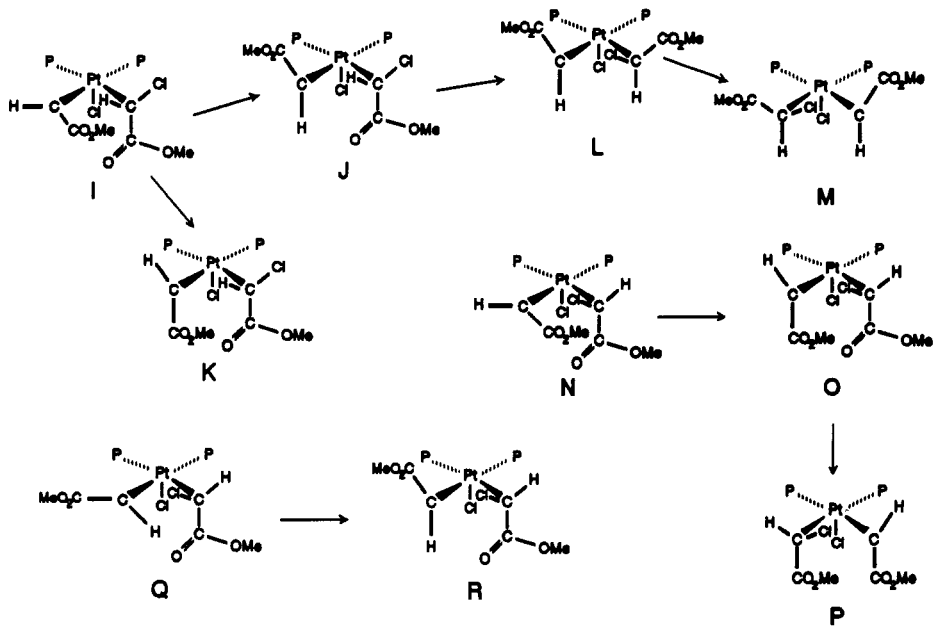
Formation of Bis-Insertion Products from [(COD)-$PtCl_2$] (1). Mechanistic arguments analogous to those used above to explain the outcome of reacting chiraphos complexes **5a–c** with diazo ester **2d** also appear valuable in rationalizing the stereochemical outcome when the products of monoinsertion from **1** that already contain a chiral center (**3b–d**) are treated with diazo derivatives **2b–d**. In each case the *R,R/S,S* pair predominates over the *R,S* diastereomer, particularly for **3b,c** reacting with **2b,c**. The preferred conformation of the *R* isomer of all of these monoinsertion products is likely[32] to be that depicted by S in Scheme III, with the bulkiest substituent (R) on the α-C essentially "axial" and the other two substituents "equatorial", the smaller one pointing diagonally in toward the complexed Cl. The diazo compound, $R'CHN_2$, would be expected to approach the less hindered face giving, *via* intermediates akin to B or H (Scheme I), the carbenes T and U. In the formation of T and U the carbene-fragment substituents (H and R') must travel past an α-CH and an olefinic CH, the former of which appears to pose the greater steric demand, being closer to the platinum. Thus, the formation of T should be somewhat easier. Capture of the displaced chloride by T produces the *R,R/S,S* pair, which is indeed found to be the preferred product of bis insertion.

An early intermediate of type H seems to better rationalize the observed preference for formation of the *R,R/S,S* pair than one of type B. With the latter, in contrast to the situation with the chiraphos ligand, there

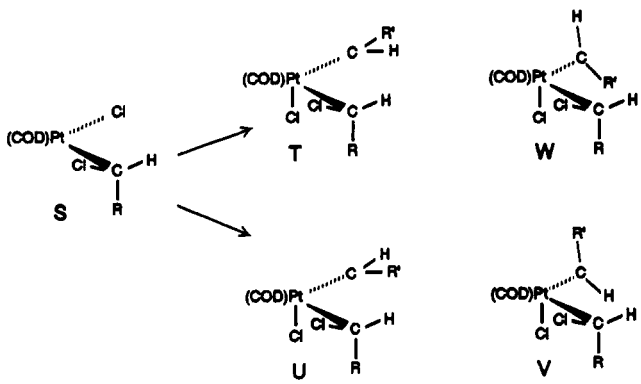
(31) HCl generated as a result of the intervention of water would react with the diazo ester. Indeed, ^1H NMR spectra of reaction mixtures involving **2d** show resonances ascribable to methyl chloroacetate. HCl generated upon cyclization of the mixed chloromethyl derivatives **4h,i** to platinaoxaphospholanes **6c,d** and platinalactone **8b** is presumably responsible for formation of the accompanying cleavage products **3c,a**, respectively.

(32) A recent X-ray structural study shows that this is indeed the case for **3c**, at least in the solid state: Ferguson, G.; Gallagher, J. F., unpublished data. A similar conformation is found in **4c**[5a] and "axial" disposition of bulky substituents is demonstrated by the X-ray crystal structure of a bis(neopentyl)platinum complex: Saare, A.; Dahlenburg, L. *Z. Naturforsch., B* **1992**, *47B*, 247–252.

Scheme II



Scheme III



is no obvious reason for one of the possible orientations of an axial carbene species to be preferred. Selectivity would then have to arise through rotation of the initially formed carbene species as it drops into the coordination plane. Closure of T or U to cyclic products (**6a,b** and **8a**) requires prior rotation of the carbene fragment to species V and W followed by intramolecular nucleophilic attack on the carbenoid carbon by the neighboring $P(O)(OMe)_2$ or CO_2Me. Of V and W, V should be preferred since, in W, the two bulky groups (R and R′) and the "axial" Cl are juxtaposed. Indeed, the trans geometry assigned (see earlier) to the major isomer in the platinalactone mixture **8a** is consistent with its formation *via* an intermediate of type V. Similarly, the $P(O)(OMe)_2$ and Cl substituents in the major platinaoxaphospholane (**6b**) obtained from reaction of **1** with diazophosphonate **2c** would be expected to be mutually trans.

Two major factors may contribute to the generation of substantially less lactone from the COD complex **1** than from the phosphine complex **5a** upon reaction with diazo ester **2d**. First, because of the greater electron-donating capacity of the phosphine, as compared with COD, carbenes derived from **5a** should be stabilized (Pt better π-donor to carbene fragment) relative to those from **1**. The phosphine-containing carbenes should then have longer lifetimes and therefore greater opportunity to undergo rotation allowing ring closure. Second, as indicated previously, the greater steric demands of the phosphine ligand may block return of the axial chlorine.

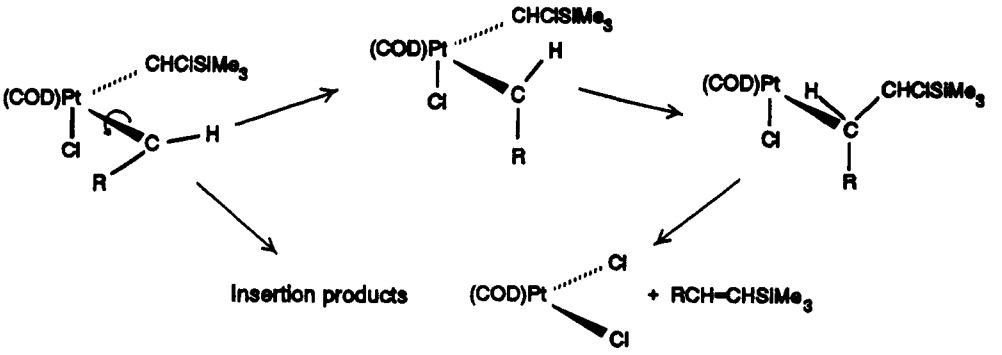
Relative Rates of Reaction. The relative rates of reaction of the four diazo compounds (**2a–d**) with the four products of monoinsertion into **1** (**3a–d**) can be rationalized on the basis of the nucleophilicity and steric size of the diazo reagent and the steric hindrance exerted by groups already bonded to the metal.

In the mechanisms discussed above, the initial attack consists of either a 1,3-dipolar cycloaddition or a step analogous to the first one in a nucleophilic displacement reaction. In either case, one would anticipate that, in the absence of potent steric effects, this attack would be more favorable, the more nucleophilic the diazo reagent.[1e] That a step of this type is important to the reaction rate appears to be borne out by the fact that the two reagents **2a,b**, which are more nucleophilic, react much more rapidly than **2c,d** with, for example, the mono(chloromethyl) complex **3a**. The diazo ester, **2d**, should be less nucleophilic than the diazophosphonate, **2c**, and the latter appears to be slightly more reactive in these insertions.

Steric demands of the larger three diazo compounds only become important when ligands that are themselves sterically demanding are present. Thus, for example, **2c** reacts rapidly with **1** or **3a** but much more slowly with either **3b** or **5a**.[33] It is perhaps not surprising that the rate of reaction with **5a** is low, since the chiraphos ligand partially blocks both faces. The reluctance of **2c** to react with **3b** is more informative, since one face of the latter is expected (see above) to be relatively open to attack. Thus, if the types of mechanism discussed above are operative, then the reaction rate must depend to some extent on the ease with which the carbene carbon can be maneuvered into the equatorial plane. It is noteworthy that the four products of monoinsertion from **1** show the following relative rates of reaction with **2c**: **3a** > **3d** > **3c** > **3b**. This reveals that, in these substrates, the predominant effect on the reaction rate exerted by the R group in the PtCHClR moiety is indeed steric, rather than

(33) **2c** is an appropriate choice for comparing relative rates of insertion since, in contrast to **2b,d**, it suffers only minimal amounts of oligomerization under these conditions.

Scheme IV



electronic, since the order of decreasing reactivity shown above parallels the order of increasing size of the relevant R group. Since an increase in electron density on the metal in the equatorial plane would be expected to favor migration of the carbene into the plane, if the electronic effect of the R group outweighed the steric effect the following reactivity order would ensue: **3b** > **3a** > **3c** > **3d**.[34] The observation that **2c** is not rapidly consumed by side reactions may indicate that this steric effect is better rationalized by the involvement of intermediates of type H (Scheme I) rather than of type B in these insertion reactions.

Formation of Olefinic and Other Byproducts. The olefinic byproducts of these insertion reactions are probably also produced *via* intermediate carbenes.[35] We have not attempted to separate and identify the products of "decomposition" of the four diazo compounds used but have noticed the following. In reactions with COD-containing complexes, excess **2a,b** decomposes within hours, even at 0 °C, while **2d** survives for several days and **2c** for several weeks at room temperature. **2b**, which contains the bulky trimethylsilyl group, yields *trans*-1,2-bis(trimethylsilyl)ethene as the only olefinic product[36] detected by ^1H NMR spectroscopy,[37] while **2d** gives a mixture of dimethyl fumarate and dimethyl maleate in essentially equimolar proportions. We also observed that **2d** underwent much slower decomposition in reactions with **5a–c**, presumably because formation of the appropriate intermediate(s) is hindered due to the bulk of the chiraphos ligand.

Dimerization is generally believed[35] to involve nucleophilic attack of a molecule of diazo compound on a previously formed electrophilic metal carbenoid species. In the present investigation, carbenoid species of types B–D (Scheme I), or analogues in which in-plane Cl is replaced by CHClR, are possible intermediates. Our results indicate that in-plane carbenoid intermediates of types C and/or D undergo very rapid intramolecular reactions (within the time of rotation about Pt–C bonds), suggesting that they are not major participants in the dimerization pathway(s). This implies that dimerization involves "axial" carbenoid intermediates such as B (or a related trigonal-bipyramidal species with an equatorial carbene ligand). Some support for this conclusion is provided by a previous observation[10] that [(COD)Pt(CH_2-$Cl)_2$] (**4a**) catalyzes formation of ethylene from diazomethane. This would be most simply explained if an axial site in **4a** behaves as a Lewis acid site,[1d] allowing initial formation of a species analogous to A.[38] Formation of intermediates of type A from $RCHN_2$ should be most favorable when R is electron-donating and is of low steric demand, in agreement with the observed relative rates of formation of dimerization/oligomerization products from **2a–d**. The reluctance of **2c** to participate in these types of processes is consistent with the large bulk and electron-withdrawing nature of the $P(O)(OMe)_2$ moiety.

In reactions of the monosilyl derivative **3b** with **2c,d** the expected mixed bis-insertion products were accompanied by small amounts of the diesters **4c,d** and bisphosphonates **4e,f**, respectively. The samples of **3b** used contained no detectable quantities of [(COD)$PtCl_2$]. However, the latter could be generated as shown in Scheme IV *via* an intramolecular migration of the $Me_3SiCHCl$ group to the neighboring carbene carbon followed by β-Cl elimination. Such a process should be particularly favorable for the two examples found in this investigation since both rotation of the in-plane carbenoid intermediate to the perpendicular orientation and the subsequent migration step would be accelerated by the steric requirements of the $Me_3SiCHCl$ group. In addition, the presence of the electron-releasing Me_3Si moiety should also favor the migration step. A sequence of this type may be at least partially responsible for the formation of *trans*-1,2-bis-(trimethylsilyl)ethene upon reaction of **3b** with the diazosilane **2b**.

When monoinsertion products **3a–d** are reacted with (trimethylsilyl)diazomethane, the resulting solutions contain not only the expected bis-insertion products but also the corresponding complexes containing a CH_2Cl group in place of $CHClSiMe_3$. The relative amounts of the two types of product do not change when the solutions are allowed to stand (although we have observed some hydrodesilylation during TLC separations). Thus, it appears that these chloromethyl derivatives are direct products of reaction rather than the result of subsequent

(34) $SiMe_3$ is expected to be electron donating when compared with H (see *e.g.*: Bock, H.; Seidl, H. *J. Organomet. Chem.* **1968**, *13*, 87–102). Any electronic effect from R on the metal atom would, of course, be attenuated by the intervening carbon atom.

(35) (a) Ishiguro, K.; Ikeda, M.; Sawaki, Y. *J. Org. Chem.* **1992**, *57*, 3057–3066. (b) Woo, L. K.; Smith, D. A. *Organometallics* **1992**, *11*, 2344–2346. (c) Onaka, M.; Kita, H.; Izumi, Y. *Chem. Lett.* **1985**, 1895–1898. (d) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277–2280. (e) Oshima, T.; Nagai, T. *Tetrahedral Lett.* **1980**, *21*, 1251–1254. (f) Nakamura, A.; Koyama, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 593–595. (g) Armstrong, R. K. *J. Org. Chem.* **1966**, *31*, 618–620.

(36) Certain complexes of osmium that convert ethyl diazoacetate into diethyl maleate and fumarate, catalytically, do not promote the production of olefins from (trimethylsilyl)diazomethane.[35b]

(37) (a) Grignon-Dubois, M.; Laguerre, M. *Organometallics* **1988**, *7*, 1443–1446. (b) Dunogues, J.; M'Gabe, D.; Laguerre, M.; Duffant, N.; Calas, R. *Organometallics* **1982**, *1*, 1525–1528.

(38) A dimerization pathway involving migration of a CH_2Cl group onto a carbene carbon followed by β-Cl elimination was excluded in this case by the observation that the **4a** recovered after treatment with excess CD_2N_2 did not contain deuterium.

hydrodesilylation. One possible explanation involves the intervention of ubiquitous water. The expected insertion products should result from axial chloride migration in intermediates of types T and U (Scheme III, R′ = $SiMe_3$). Because of the steric requirements of R′ in this case, intermediates V and W, in which direct chloride migration is stereoelectronically unfavorable, should be preferred. The relatively electrophilic Si in these intermediates may be susceptible (and more accessible than the carbene C) to attack by an external nucleophile such as water. This type of attack, accompanied by proton transfer to the α-C, would give the corresponding methylene carbene and subsequently chloromethyl product by carbene rotation, if necessary, and chloride migration. The reaction mixtures obtained from **3c,d** also show ^{31}P and ^{1}H NMR signals, respectively, indicating the presence of small amounts of platinaoxaphospholanes **6c,d** and platinalactones **8b,c**. If the cyclization mechanisms proposed above are correct, these products are formed by internal attack on intermediates of type V and W, the first three after hydrodesilylation. The product ratios found would imply that both hydrodesilylation and formation of CH_2Cl derivatives are faster than cyclization. Finally, the fact that we could find no ^{31}P NMR signals attributable to Me_3Si-containing platinaoxaphospholanes (i.e. products analogous to **8c**) may reflect a greater steric barrier for the $P(O)(OMe)_2$ *vs* the CO_2Me substituent to the adoption of an appropriate conformation for cyclization.

Conclusions

(i) Monoinsertion products can be produced from [(COD)$PtCl_2$] and diazo compounds of the type $RCHN_2$, where R may be electron-donating or -withdrawing and also relatively bulky. (ii) Both symmetrical and unsymmetrical simple bis-insertion products can also be obtained by similar reactions. (iii) For simple bis-insertion products having two chiral α-C atoms, the yield of *R,R/S,S* isomer outweighs that of the *R,S* isomer. (iv) Simple bis-insertion products are generally accompanied by other platinum-containing derivatives formed, for example, by cyclization. (v) [{(*R,R*)-chiraphos}$PtCl_2$] reacts with $RCHN_2$ to give mono-insertion products in which the *R* configuration is preferred for the new chiral center. (vi) [{(*R,R*)-chiraphos}-$PtCl_2$] gives only minor amounts of simple bis-insertion products upon reaction with N_2CHCO_2Me, the major products being platinalactones. (vii) The nature and stereochemistry of the products of the reactions in (i)–(vi), and the relative rates of some of these reactions, can be rationalized by proposing the involvement of three related types of carbenoid intermediates.

Experimental Section

Spectral data were acquired as follows: IR spectra, Bomen MB-100 (CH_2Cl_2 solution); ^{1}H and ^{13}C NMR spectra, Varian UNITY 400 or Gemini 200 ($CDCl_3$ solution, residual proton resonance at δ 7.24 and carbon resonance at δ 77.0 as references); ^{31}P NMR spectra, Varian UNITY 400 ($CDCl_3$ solution unless indicated otherwise, phosphorus resonance of triphenylphosphine in $CDCl_3$ at δ −5.3 as external reference). Immediately prior to use, $CDCl_3$ was passed through a short plug of anhydrous potassium carbonate. ^{1}H NMR data required for the discussion and ^{31}P NMR data are collected in Tables I and II, respectively. ^{13}C and additional ^{1}H NMR data are given below. Elemental analyses were determined by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Diazomethane (**2a**) was prepared by reacting *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide with potassium hydroxide in aqueous 2-(2-ethoxyethoxy)ethanol and was distilled in diethyl ether. Dimethyl (diazomethyl)phosphonate (**2c**)[39] and methyl diazoacetate (**2d**)[40] were obtained by published methods. (Trimethylsilyl)diazomethane (2 M in hexane), [(COD)$PtCl_2$], 1,2-bis(diphenylphosphino)ethane, and (*R,R*)-chiraphos were commercial products (Aldrich) and were used as received. Analytical- and preparative-scale thin-layer chromatography (TLC) was performed on Kieselgel G (Merck). Silica gel for flash chromatography (Fisher, 230–425 mesh) was used for short-column cleanup of reaction mixtures.

Reactions of the Complexes with the Diazo Compounds. Reactions, with the exceptions indicated below, were carried out at room temperature in subdued light but without precautions to exclude air or moisture.

Reaction of [(COD)$PtCl_2$] (1) with (Trimethylsilyl)diazomethane (2b). (i) Reaction of 1 (74.8 mg, 0.20 mmol) in dichloromethane (5 mL) with **2b** in hexane (0.20 mL, 0.40 mmol) for 10 min gave a product mixture that showed essentially a single spot of R_f higher than that of 1 on TLC. The resulting solution was passed through a short column of silica gel (2 g) that was then washed with dichloromethane. The eluate was evaporated to give a solid (90.0 mg) that proved to be essentially pure chloro[chloro(trimethylsilyl)methyl](1,5-cyclooctadiene)platinum(II) (**3b**) as judged by its ^{1}H and ^{13}C NMR spectra. Purification by preparative TLC (dichloromethane) followed by crystallization from dichloromethane/pentane gave colorless needles: mp 116–126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.22 (s, 9 H, Me), 4.81 (m, J_{Pt-H} = 72 Hz, 1 H), 4.96 (m, J_{Pt-H} = 78 Hz, 1 H), 5.48 (m, J_{Pt-H} = 43 Hz, 1 H), 5.59 (m, J_{Pt-H} = 37 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.6 (J_{Pt-C} = 43.5 Hz), 112.3 (J_{Pt-C} = 36.5 Hz), 97.1 (J_{Pt-C} = 236.5 Hz), 86.9 (J_{Pt-C} = 205.2 Hz), 53.6 (J_{Pt-C} = 744.7 Hz), 32.8 (J_{Pt-C} = 19.1 Hz), 29.8 (J_{Pt-C} = 20.6 Hz), 28.8 (J_{Pt-C} = 26.7 Hz), 27.4 (J_{Pt-C} = 13.7 Hz), 0.53 (J_{Pt-C} = 10.1 Hz). Anal. Calcd for $C_{12}H_{22}Cl_2PtSi$: C, 31.31; H, 4.82. Found: C, 31.61; H, 4.59.

(ii) Crystalline **3b** (40.5 mg, 0.088 mmol) was dissolved in dichloromethane (0.5 mL), and **2b** in hexane (0.15 mL, 0.30 mmol) was added. TLC of the solution after 4 days showed a major spot with an R_f corresponding to starting material and a very faint, less polar spot. Preparative TLC of this mixture (dichloromethane) gave **3b** (27.2 mg) and a less polar fraction (2.0 mg), the ^{1}H NMR spectrum of which was dominated by aliphatic- and SiMe-type resonances and contained only relatively insignificant peaks attributable to Pt-containing compounds.

(iii) A solution of **3b** (36.5 mg, 0.079 mmol) in $CDCl_3$ (2 mL) was cooled to −78 °C, and **2b** in hexane (0.23 mL, 0.46 mmol) was added. A ^{1}H NMR spectrum of a portion of this solution run, immediately, at −17 °C contained only resonances attributable to the two reactants. A second spectrum, run after 20 min, contained a relatively minute singlet at δ 3.63, arising from **4b**. The solution was then warmed up, progressively, to −5, −1, and 7 °C and spectra were run 10 min after the temperature had stabilized (this required *ca.* 8 min) in each case. These spectra revealed a progressive increase in the intensity of the peak at δ 3.63, but a number of new peaks appeared in the −5 °C spectrum, including singlets at δ 0.045 and 6.56 (J_{Si-H} = 9.5 Hz), due to *trans*-1,2-bis(trimethylsilyl)ethene[37] and the intensity of these signals, relative to the one at δ 3.63, increased markedly at 7 °C. This NMR sample, and the main sample, were then kept in an ice bath for 16 h. A ^{1}H NMR spectrum then showed that all of the diazo reagent had been consumed, giving a large quantity of the trans olefin (but no detectable amount of the cis isomer), and that *ca.* 35% of **3b** had been converted into **4b**. No resonance attributable to the diastereomer of **4b** was observed, but peaks corresponding to **4g** and a singlet at δ 4.10 (J_{Pt-H} = 95 Hz) were present. Preparative TLC (dichloromethane/hexane, 1:1) of the

(39) Seyferth, D.; Mariner, R. S.; Hilbert, P. *J. Org. Chem.* **1971**, *36*, 1379–1386.
(40) Myhre, P. C.; Maxey, C. T.; Bebout, D. C.; Swedberg, S. H.; Petersen, B. L. *J. Org. Chem.* **1990**, *55*, 3417–3421.

combined products gave **3b** (17.8 mg), the less polar **4b** (5.4 mg) as a solid (^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (s, 18 H, Me), 5.05 (m, J_{Pt-H} = 35 Hz, 2 H), 5.52 (m, J_{Pt-H} = 44 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 110.9 (J_{Pt-C} = 86.6 Hz), 99.0 (J_{Pt-C} = 61.3 Hz), 59.7 (J_{Pt-C} = 881.7 Hz), 30.5, 28.7, 0.85 (J_{Pt-C} = 18.0 Hz)) and a fraction (3.3 mg) of intermediate polarity containing **4g**. The product **4b**, although stable in $CDCl_3$ for at least 10 days, decomposed (*ca.* 20%, ^{1}H NMR evidence) to **1** when left as the solid in a refrigerator for 3 days.

Reaction of [(COD)PtCl$_2$] with Dimethyl (Diazomethyl)-phosphonate (2c). (i) Solid **1** (74.8 mg, 0.20 mmol) dissolved rapidly when stirred with a solution of **2c** (34.0 mg, 0.23 mmol) in dichloromethane (2 mL). After 15 min, TLC showed a small spot for **1**, a major, more polar spot, and a trace of even more polar material. The major product, chloro[chloro(dimethoxyphosphonyl)methyl](1,5-cyclooctadiene)platinum(II), **3c** (89.1 mg), was recovered by preparative TLC (dichloromethane/methanol, 19:1). Crystallization from dichloromethane/pentane gave colorless rectangular blocks: mp 105–107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.73 (d, J_{P-H} = 10.4 Hz, 3 H, Me), 3.74 (d, J_{P-H} = 10.4 Hz, 3 H, Me), 5.15 (m, J_{Pt-H} = 72 Hz, 1 H), 5.30 (s, CH_2Cl_2 in crystals), 5.57 (m, J_{Pt-H} = 48 Hz, 1 H), 5.69 (m, J_{Pt-H} = 45 Hz, 1 H), 5.78 (m, J_{Pt-H} = 72 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 113.5 (J_{Pt-C} = 61.1 Hz), 113.3 (J_{Pt-C} = 47.8 Hz), 99.4 (J_{Pt-C} = 207.6 Hz), 93.7 (J_{Pt-C} = 172.0 Hz), 54.3 (J_{P-C} = 7.2 Hz), 54.2 (J_{P-C} = 7.8 Hz), 40.6 (J_{P-C} = 135.6 Hz, J_{Pt-C} = 821.5 Hz), 33.9 (J_{Pt-C} = 15.9 Hz), 30.0 (J_{Pt-C} = 13.3 Hz), 29.9 (J_{Pt-C} = 21.8 Hz), 27.7 (J_{Pt-C} = 10.2 Hz). Anal. Calcd for $C_{11}H_{19}Cl_2O_3PPt\cdot0.6CH_2Cl_2$: C, 25.46; H, 3.72. Found: C, 25.37; H, 3.63.

(ii) When **1** (93.5 mg, 0.25 mmol) was dissolved, with agitation, in a solution of **2c** (151 mg, 1.00 mmol) in dichloromethane (4 mL), TLC of the reaction mixture after 3 days showed only spots more polar than **3c**. A ^{31}P NMR spectrum of this mixture contained resonances for unreacted diazophosphonate, bis-insertion products **4c,d**, platinaoxaphospholanes **6a,b** and a third isomer (δ_P 46.3 (J_{P-P} = 29.5 Hz, J_{Pt-P} = 145.0 Hz) and 29.3 (J_{P-P} = 29.5 Hz, J_{Pt-P} = 30 Hz)), and the oligomeric species **7**. Preparative TLC (dichloromethane/methanol, 23:2) of the product mixture afforded essentially pure samples of the following compounds, which are dealt with in increasing order of polarity. (a) The least polar band contained reagent **2c** (62.0 mg). (b) (*R,R/S,S*)-bis[chloro(dimethoxyphosphonyl)methyl](1,5-cyclooctadiene)platinum(II) (**4c**; 84.8 mg) crystallized from diethyl ether as colorless prisms: mp 126–142 °C (premelt 76–84 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.81 (d, J_{P-H} = 10.5 Hz, 6 H, Me), 3.82 (d, J_{P-H} = 10.5 Hz, 6 H, Me), 5.52 (m, J_{Pt-H} = 50 Hz, 2 H), 6.02 (m, J_{Pt-H} = 37 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 113.1 (J_{Pt-C} = 94 Hz), 106.9 (J_{Pt-C} = 66 Hz), 54.0 (J_{P-C} = 7 Hz), 53.7 (J_{P-C} = 6.5 Hz), 45.3 (J_{P-C} = 131 Hz, J_{Pt-C} = 890 Hz), 32.8, 25.4. Anal. Calcd for $C_{14}H_{26}Cl_2O_6P_2Pt\cdot2H_2O$: C, 25.70; H, 4.62. Found: C, 25.28; H, 4.38. (c) (*R,S*)-bis[chloro(dimethoxyphosphonyl)methyl](1,5-cyclooctadiene)platinum(II) (**4d**; 24.3 mg) crystallized from diethyl ether/pentane as colorless prisms: mp 132–136 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.76 (d, J_{P-H} = 11.0 Hz, 6 H, Me), 3.84 (d, J_{P-H} = 11.0 Hz, 6 H, Me), 5.52 (m, J_{Pt-H} = 46 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 109.1 (J_{Pt-C} = 80.4 Hz), 106.3 (J_{Pt-C} = 73.0 Hz), 54.5 (J_{P-C} = 7.3 Hz), 53.7 (J_{P-C} = 6.9 Hz), 39.9 (J_{P-C} = 133.1 Hz, J_{Pt-C} = 931.7 Hz), 30.1, 29.6. Anal. Calcd for $C_{14}H_{26}Cl_2O_6P_2Pt\cdot H_2O$: C, 26.42; H, 4.44. Found: C, 26.67; H, 4.45. (d) The minor 4-platina-1,2-oxaphospholane **6a** (6.2 mg) had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.78 (d, J_{P-H} = 10.5 Hz, 3 H, *exo*-POMe), 3.82 (d, J_{P-H} = 10.7 Hz, 3 H, *exo*-POMe), 3.84 (d, J_{P-H} = 10.5 Hz, 3 H, *endo*-POMe), 5.30 (m, J_{Pt-H} obscured, 1 H), 5.31 (m, J_{Pt-H} obscured, 1 H), 5.48 (m, J_{Pt-H} = 44 Hz, 1 H), 6.08 (m, J_{Pt-H} = 43 Hz, 1 H). (e) The major 4-platina-1,2-oxaphospholane **6b** (19.3 mg) had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.73 (d, J_{P-H} = 10.0 Hz, 3 H, *exo*-POMe), 3.80 (d, J_{P-H} = 10.0 Hz, 3 H, *exo*-POMe), 3.80 (d, J_{P-H} = 10.0 Hz, 3 H, *endo*-POMe), 5.33 (m, J_{Pt-H} obscured, 1 H), 5.42 (m, J_{Pt-H} obscured, 1 H), 5.47 (m, J_{Pt-H} obscured, 1 H), 6.01 (m, J_{Pt-H} = 43 Hz, 1 H) and ^{13}C NMR ($CDCl_3$, 100 MHz) δ 111.5 (J_{Pt-C} = 93.1 Hz), 107.0 (J_{Pt-C} = 61.7 Hz), 106.3 (J_{Pt-C} = 56.0 Hz), 105.2 (J_{Pt-C} = 87.0 Hz), 62.5 (J_{P-C} = 151.1, 9.2 Hz, J_{Pt-C} = 789.0 Hz), 54.6 (J_{P-C} = 7.6 Hz), 52.8 (J_{P-C} = 6.1 Hz, 2 C's), 48.2 (J_{P-C} = 126.7 Hz, J_{Pt-C} = 879.0 Hz), 31.4, 31.3, 27.7, 26.9. (f) The polynuclear complex **7** (10.3 mg) had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (d, J_{P-H} = 10.4 Hz, 6 H), 3.81 (d, J_{P-H} = 10.4 Hz, 3 H), 3.83 (d, J_{P-H} = 10.4 Hz, 3 H), 3.84 (d, J_{P-H} = 10.4 Hz, 3 H), 3.85 (d, J_{P-H} = 10.4 Hz, 3 H), 3.88 (d, J_{P-H} = 10.4 Hz, 3 H), 5.29, 5.43, 5.52, 5.58, 5.96, 6.01 and 6.23 (each m, 1 H) and ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.8, 110.3, 107.9, 107.1, 106.9, 104.0, 102.9, 102.7 (olefinic C's), 65.9 (α-C, J_{P-C} = 136.5 Hz), 64.3 (α-C, J_{P-C} = 151.8, 10.0 Hz), 54.5, 53.5, 53.45, 53.15, 53.1, 52.9, 52.6 (poorly resolved, OMe C's, J_{P-C} = *ca* 7 Hz for each), 44.3 (α-C, J_{P-C} = 125.5 Hz), 41.0 (α-C, J_{P-C} = 125.5 Hz), 32.4, 32.0, 31.6, 31.4, 27.8 (2 × C), 26.4, 25.8 (allylic C's).

Reaction of [(COD)PtCl$_2$] with Methyl Diazoacetate (2d). (i) [(COD)PtCl$_2$] (74.8 mg, 0.20 mmol) was dissolved in a solution of methyl diazoacetate (25.5 mg, 0.22 mmol) in dichloromethane (2.5 mL) with stirring. After 40 min, TLC of the resulting mixture showed only spots more polar than that of **1** and this mixture was submitted to preparative TLC (dichloromethane/methanol, 99:1). This gave a main band containing essentially pure chloro[chloro(methoxycarbonyl)methyl](1,5-cyclooctadiene)platinum(II) (**3d**; 78.3 mg) and more polar material (7.9 mg; total extract from several weak bands). The material from the main band crystallized from dichloromethane/pentane as colorless prisms: mp 143–146 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.74 (s, 3 H, Me), 4.91 (m, J_{Pt-H} = 72 Hz, 1 H), 5.13 (m, J_{Pt-H} = 72 Hz, 1 H), 5.74 (m, J_{Pt-H} = 42 Hz, 1 H), 5.75 (m, J_{Pt-H} = 42 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 174.0, 114.0 (J_{Pt-C} = 54.1 Hz), 113.95 (J_{Pt-C} = 54.0 Hz), 94.9 (J_{Pt-C} = 205.0 Hz), 92.4 (J_{Pt-C} = 194.4 Hz), 52.7, 45.2 (J_{Pt-C} = 643.3 Hz), 32.5 (J_{Pt-C} = 17.9 Hz), 31.3 (J_{Pt-C} = 17.5 Hz), 29.0 (J_{Pt-C} = 17.8 Hz), 28.3 (J_{Pt-C} = 14.8 Hz). Anal. Calcd for $C_{11}H_{16}Cl_2O_2Pt$: C, 29.61; H, 3.61. Found: C, 29.63; H, 3.32.

(ii) A solution of **1** (74.8 mg, 0.20 mmol) and **2d** (120 mg, 1.0 mmol) in dichloromethane (3 mL) was left at ambient temperature for 1 week. A ^{1}H NMR spectrum of the product showed the presence of broadly similar amounts of **3d**, **4e,f**, and **8a**. This mixture was redissolved in dichloromethane (3 mL) and more of the diazo ester added (60.0 mg, 0.50 mmol). After 1 week, the product mixture still contained **3d** (*ca.* 10%) (^{1}H NMR spectroscopy) and this mixture was exposed to a further amount of **2d** (60.0 mg) in dichloromethane for an additional 1 week. Examination of the product, as before, revealed the presence of **3d** (<10%). Separation of this mixture by preparative TLC (dichloromethane/methanol, 1:199, run twice) gave the following fractions in decreasing order of polarity. (a) A material (5.9 mg) was obtained that showed very broad signals in its ^{1}H NMR spectrum, including some from (COD)Pt moieties. (b) A fraction (9.6 mg) was isolated containing largely the ester lactone **8a**, which was purified by further preparative TLC (dichloromethane/methanol, 1:49): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.72 (s, 3 H, Me, major isomer), 3.75 (s, Me, minor isomer, *ca.* 0.1 × intensity of 3.72 peak), 5.0–5.6 (overlapping m's, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 180.5, 174.4, 111.5 (J_{Pt-C} = 86.0 Hz), 106.7 (2 × C, J_{Pt-C} = 66.3 Hz), 105.7 (J_{Pt-C} = 70.2 Hz), 70.1 (J_{Pt-C} = 720.5 Hz), 59.2 (J_{Pt-C} = 922.5 Hz), 52.3, 31.9, 31.6, 28.3, 27.6; IR (dichloromethane) 1743 (C=O, ester), 1725 (C=O, lactone) cm^{-1}. (c) A fraction (28.1 mg) consisting largely of (*R,S*)-bis[chloro(methoxycarbonyl)methyl](1,5-cyclooctadiene)platinum(II) (**4f**) was obtained, along with small amounts of **3d** and **4e**. Purification by preparative TLC (dichloromethane/methanol, 1:199, run thrice) and crystallization from dichloromethane/pentane gave colorless prisms (which still contained traces of **3d** (^{1}H NMR spectroscopy)) of **4f**: mp 145–147 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.70 (s, J_{Pt-H} = 4 Hz, 6 H, Me), 5.20 (m, J_{Pt-H} obscured, 2 H), 5.65 (m, J_{Pt-H} obscured, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 175.0, 108.0 (J_{Pt-C} = 78.5 Hz), 106.6 (J_{Pt-C} = 75.9 Hz), 52.4, 47.0 (J_{Pt-C} = 850.1 Hz), 30.1, 29.6. Anal. Calcd for $C_{14}H_{20}Cl_2O_4Pt\cdot0.1C_5H_{12}$: C, 33.14; H, 4.07. Found: C, 33.42; H, 3.76. (d) A solid fraction (26.9 mg) of essentially pure (*R,R/S,S*)-bis[chloro(methoxycarbonyl)methyl](1,5-cyclooctadiene)platinum(II) (**4e**) was isolated, contaminated with traces of **3d**. Crystallization of this solid from dichloromethane/pentane gave colorless prisms (which still

contained detectable (^{1}H NMR spectroscopy) traces of **3d**): mp 142 °C (premelt 116–118 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.75 (s, 6 H, Me), 5.28 (CH_2Cl_2 in crystals), 5.4–5.85 (m's, J_{Pt-H} obscured, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 174.4, 111.5 (J_{Pt-C} = 88.5 Hz), 106.9 (J_{Pt-C} = 68.0 Hz), 52.6, 50.5 (J_{Pt-C} = 832.8 Hz), 32.4, 26.6. Anal. Calcd for $C_{14}H_{20}Cl_2O_4Pt \cdot 0.25CH_2Cl_2$: C, 31.72; H, 3.83. Found: C, 31.70; H, 3.83.

(iii) The reaction of a sample of **1** (18.7 mg, 0.050 mmol) with methyl diazoacetate (30 mg, 0.30 mmol) in $CDCl_3$ (0.75 mL) was monitored by ^{1}H NMR spectroscopy. After 2.5 h the signals for **1** had been replaced by those for **3d** (*ca.* 90%), **4e** (*ca.* 5%), and **4f** (*ca.* 5%). After 24 h these same three products were present in an approximate ratio of 1:1:1. One day later the ratio **4e:4f:3d** was about 5:4:1 and over 90% of the diazo ester had been consumed. After 4 days more nearly all of the **3d** had been converted into bis-insertion products and none of the diazo reagent remained. In all of these spectra, olefinic peaks from dimethyl fumarate (δ 6.82) and maleate (δ 6.22) were present and weak signals from **8a** were seen in spectra run after reaction times of at least 24 h.

Reaction of the Monoinsertion Products 3b–d with Diazomethane (2a). A chilled solution of diazomethane in diethyl ether was added dropwise, over several minutes, to **3b** (49.5 mg, 0.11 mmol) in dichloromethane (3 mL) at 0 °C until a pale yellow color persisted. When this solution was warmed to room temperature, the color rapidly dissipated, and a waxy precipitate formed. The resulting solution was passed through a short column of silica (2 g), which was then washed with dichloromethane. Evaporation of the solvent from the combined eluates gave essentially pure (^{1}H NMR spectroscopy) **4g**, which, when subjected to preparative TLC (pentane/dichloromethane, 1:4) showed only a single, strong band of R_f 0.8. The material (25.5 mg) recovered from this band had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.18 (s, 9 H, Me), 5.22 (m, J_{Pt-H} = 44 Hz, 1 H), 5.24 (m, J_{Pt-H} obscured, 1 H), 5.28 (m, J_{Pt-H} obscured, 1 H), 5.46 (m, J_{Pt-H} = 44 Hz, 1 H).

A solution of **3c** (67.1 mg, 0.14 mmol) in dichloromethane (8 mL) was cooled in an ice bath and treated with diazomethane in diethyl ether in two aliquots (each 1 mL, *ca.* 0.3 mmol). Rapid gas evolution and decoloration was observed during the addition of the first aliquot. Decoloration of the second aliquot required several minutes and was accompanied by precipitation of a fine, colorless solid. Solvent was removed, *in vacuo*, and the residue extracted with dichloromethane (3 mL). The resulting suspension was run onto a short column of silica, and the column was eluted with dichloromethane/methanol (49:1, 12 mL) followed by dichloromethane/methanol (19:1, 12 mL). The resulting eluates were evaporated, *in vacuo*, and gave residues of 76.7 and 2.0 mg, respectively. Preparative TLC (dichloromethane/methanol, 49:1) of the former gave a less polar gum (53.1 mg) and a more polar solid (9.2 mg). The less polar fraction was essentially pure, "mixed" bis-insertion product **4h** which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.76 (d, J_{P-H} = 10.7 Hz, 3 H, Me), 3.81 (d, J_{P-H} = 10.7 Hz, 3 H, Me), 5.19 (m, J_{Pt-H} = 51 Hz, 1 H), 5.32 (m, J_{Pt-H} = 42 Hz, 1 H), 5.58 (m, J_{Pt-H} = 38 Hz, 1 H), 5.96 (m, J_{Pt-H} = 38 Hz, 1 H). After the sample sat as a gum at ambient temperature for 4 weeks, its ^{1}H NMR spectrum contained only weak resonances for **4h** but relatively strong ones for platinaoxaphospholane **6c**, as did the spectrum of the 2-mg fraction from the original column and the more polar fraction from preparative TLC. All three samples were combined and submitted to preparative TLC (dichloromethane/methanol, 47:3). This gave the following three fractions, in order of increasing polarity: (a) the monophosphonate **3c** (27.6 mg); (b) the 4-platina-1,2-oxaphospholane **6d** (4.6 mg), which had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (d, J_{P-H} = 10.8 Hz, 3 H, Me), 4.73 (m, J_{Pt-H} obscured, 1 H), 4.77 (m, J_{Pt-H} obscured, 1 H), 5.37 (m, J_{Pt-H} = 40 Hz, 1 H), 5.42 (m, J_{Pt-H} = 44 Hz, 1 H); (c) the isomeric, major, 4-platina-1,2-oxaphospholane **6c** (23.2 mg), which had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (d, J_{P-H} = 11.0 Hz, 3 H, Me), 4.73 (m, J_{Pt-H} obscured, 1 H), 4.80 (m, J_{Pt-H} obscured, 1 H), 5.44 (m, J_{Pt-H} = 40 Hz, 2 H) and ^{13}C NMR ($CDCl_3$, 100 MHz) δ 111.5 (J_{Pt-C} = 64.0 Hz), 104.7 (J_{Pt-C} = 55.8 Hz), 102.9 (J_{Pt-C} = 84.2 Hz), 99.5 (J_{Pt-C} = 84.2 Hz), 60.6 (J_{P-C} = 7.3 Hz, J_{Pt-C} = 787.2 Hz), 54.4 (J_{P-C} = 6.4 Hz), 48.4 (J_{P-C} = 129.0 Hz, J_{Pt-C} = 934.9 Hz), 30.9, 30.6, 28.2, 27.2.

A solution of diazomethane in diethyl ether (3 mL, *ca.* 0.9 mmol) was added in three aliquots to **3d** (80.5 mg, 0.18 mmol) in dichloromethane (9 mL) at 0 °C. Rapid loss of color, along with gas evolution, was observed upon addition of the first two aliquots. The color persisted after the final addition, and a finely divided off-white precipitate formed. After sitting at room temperature overnight, the reaction mixture was evaporated, *in vacuo*, and the residue washed onto a short silica column in dichloromethane (3 mL). The column was then eluted with dichloromethane (12 mL) followed by dichloromethane/methanol (9:1, 12 mL). Evaporation of these eluates gave residues of 92.0 and 6.8 mg, respectively. A ^{1}H NMR spectrum of the former showed that it contained mainly the "mixed" bis-insertion product **4i**. This material was subjected to preparative TLC (dichloromethane/methanol, 199:1), which gave three major fractions that are dealt with in increasing order of polarity: (a) the monoester **3d** (11.2 mg); (b) the bis-insertion product **4i** (27.4 mg), which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.70 (s, J_{Pt-H} = 4 Hz, 3 H, Me), 5.36 (m, J_{Pt-H} = 50 Hz, 1 H), 5.46 (m, J_{Pt-H} obscured, 1 H), 5.52 (m, J_{Pt-H} obscured, 1 H), 5.57 (m, J_{Pt-H} = 40 Hz, 1 H); (c) the lactone **8b** (19.5 mg), which had ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.92 (m's, J_{Pt-H} obscured, 2 H), 5.40 (m, J_{Pt-H} = 42 Hz, 1 H), 5.58 (m, J_{Pt-H} = 41 Hz, 1 H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 111.3 (J_{Pt-C} = 65.8 Hz), 104.6 (J_{Pt-C} = 53.0 Hz), 103.9 (J_{Pt-C} = 73.4 Hz), 100.0 (J_{Pt-C} = 72.3 Hz), 63.6 (J_{Pt-C} = 786.3 Hz), 59.7 (J_{Pt-C} = 937.2 Hz), 31.2 (br), 30.7, 29.2 (J_{Pt-C} = 8.7 Hz), 28.1 (resonance for C=O C not observed) and IR (dichloromethane) 1725 (C=O) cm^{-1}.

Reaction of the Monoinsertion Products 3a,c,d with (Trimethylsilyl)diazomethane (2b). When a solution of **3a** (28.0 mg, 0.072 mmol) in CH_2Cl_2 (3 mL) was cooled to 0 °C and **2b** in hexane (0.25 mL, 0.50 mmol) added, dropwise, an initial loss of color was observed, but the final solution was a clear, pale yellow.[41] After the mixture sat in the refrigerator overnight, the solvent was evaporated and a ^{1}H NMR spectrum run. This showed peaks for a major amount of **4g** and minor amounts of **3a,b** and **4a**. Preparative TLC (hexane/dichloromethane, 1:9) gave three main fractions. The least polar of these (3.7 mg) contained largely (^{1}H NMR spectroscopy) **4g**, along with some **4a**, **3a**, and **1**. When a solution of this material in $CDCl_3$ was left at room temperature, peaks for **3a** and **1** increased in relative intensities. The next fraction (4.8 mg) was essentially pure **3b** and the most polar (4.5 mg) essentially pure **3a**.

Solutions of **3c** (31.1 mg, 0.063 mmol) in $CDCl_3$ (0.75 mL) and **2b** in hexane (0.09 mL, 0.18 mmol) were mixed at −10 °C, and the formation of products from **3c** was monitored by ^{31}P NMR spectroscopy at this temperature. Approximately 50% of the substrate was consumed in 30 min, and the temperature was then allowed to rise to 10 °C. This resulted in complete loss of the resonance for **3c** within 20 min. Peaks for **4j,h,k**, **6c,d**, and an unidentified species (δ 32.4) were present in an approximate ratio of 32:22:12:2:1:3. This mixture was separated by preparative TLC and gave the following three major fractions. (a) The least polar fraction (6.2 mg) contained essentially pure **4j**, the major, "mixed" bis-insertion product, which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.22 (s, 9 H, SiMe), 3.80 (d, J_{P-H} = 10.8 Hz, 3 H, OMe), 3.88 (d, J_{P-H} = 10.7 Hz, 3 H, OMe), 5.20 (m, J_{Pt-H} = 41 Hz, 1 H), 5.44 (m, J_{Pt-H} = 45 Hz, 1 H), 5.54 (m, J_{Pt-H} = 55 Hz, 1 H), 6.07 (m, J_{Pt-H} = 36 Hz, 1 H). (b) The fraction (1.0 mg) of intermediate polarity consisted of the minor, "mixed" bis-insertion product **4k**, which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.21 (s, 9 H, SiMe), 3.76 (d, J_{P-H} = 10.5 Hz, 3 H, OMe), 3.85 (d, J_{P-H} = 10.6 Hz, 3 H, OMe), 5.32 (m's, J_{Pt-H} obscured, 2 H), 5.81 (m, J_{Pt-H} = 40 Hz, 1 H), 5.90 (m, J_{Pt-H} = 44 Hz, 1 H). (c) The most polar fraction (4.9 mg) contained **4h**.

(Trimethylsilyl)diazomethane in hexane (0.3 mL, 0.6 mmol) was added to a solution of the monoester **3d** (53.1 mg, 0.12 mmol)

(41) A similar reaction, carried out at room temperature, rapidly produced a very murky solution.

in dichloromethane (3 mL) at 0 °C. TLC after 1 h showed that no detectable amounts of **3d** remained. The resulting solution was filtered through a short silica column, which was then washed with additional dichloromethane. A ^{1}H NMR spectrum of the yellow gum (60.8 mg; darkened on standing) obtained upon evaporation of the eluate contained resonances mainly for a major (**4l**) and a minor (**4m**) "mixed" bis-insertion product and for **4i**, in an approximate ratio of 3:2:2. This material was distributed among three preparative TLC plates, one of which was left in the dark at room temperature overnight before being developed (dichloromethane). Components present in the significant fractions from these plates were identified by ^{1}H NMR spectroscopy. The bands from the single plate were combined to give two major fractions, the more polar of which (12.4 mg from three close-running bands) contained mainly the silyl lactone **8c**, the lactone **8b**, and the monoester **3d**, while the second (4.0 mg from four bands) contained mainly **3a,b**, **4i**, and traces of **4l**. The other two plates yielded four fractions which are dealt with in decreasing order of polarity: (a) a mixture (4.2 mg) of mainly **8c** and a minor amount of **3d**; (b) essentially pure **4i** (3.4 mg); (c) a mixture (19.0 mg) of mainly **4l** along with some **4m** (*ca.* 8:1); (d) essentially pure **3b** (1.7 mg). The mixture of **4l** and **4m** had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.22 (s, 9 H, SiMe, minor isomer), 0.23 (s, 9 H, SiMe, major isomer), 3.67 (s, J_{Pt-H} = 4 Hz, 3 H, OMe, minor isomer), 3.73 (s, J_{Pt-H} = 4 Hz, 3 H, OMe, major isomer), 4.90–5.80 (m's, 4H, both isomers). A ^{1}H NMR spectrum run on the material resulting from allowing this mixture to sit as a gum at room temperature for 30 days showed that the major constituent was now **8c**. The various fractions containing **8c** were combined and subjected to preparative TLC (dichloromethane/methanol, 199:1). The major band, of R_f 0.3, contained essentially pure silyl lactone **8c**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.08 (s, 9 H, Me), 4.99 (m, J_{Pt-H} = 46 Hz, 1 H), 5.11 (m, J_{Pt-H} obscured, 1 H), 5.20 (m, J_{Pt-H} = 47 Hz, 1 H), 5.39 (m, J_{Pt-H} = 40 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 109.8 (J_{Pt-C} = 72.2 Hz), 105.3 (J_{Pt-C} = 77.1 Hz), 103.9 (J_{Pt-C} = 52.7 Hz), 99.1 (J_{Pt-C} = 67.5 Hz), 78.2 (J_{Pt-C} = 710 Hz), 60.2 (J_{Pt-C} = 963 Hz), 32.3 (br), 32.0, 28.2 (J_{Pt-C} = 9.2 Hz), 26.8, –0.015 (J_{Pt-C} = 17 Hz) (resonance for C=O C not observed); IR (dichloromethane) 1718 (C=O) cm^{-1}.

Reaction of the Monoinsertion Products 3a,b,d with Dimethyl (Diazomethyl)phosphonate (2c). The reaction of **2c** (35.0 mg, 0.23 mmol) with **3a** (11.5 mg, 0.030 mmol) in $CDCl_3$ (0.8 mL) was monitored by ^{1}H NMR spectroscopy. Resonances for only one Pt-containing product, **4h**, were observed, with *ca.* 50% conversion in 80 min and complete conversion in 16 h.

The reaction of **3b** (15 mg, 0.033 mmol) with **2c** (23 mg, 0.15 mmol) in $CDCl_3$ was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 3 weeks practically all of both reagents had been consumed and the ^{31}P spectrum contained a large number of resonances upfield of δ 25 (compounds lacking Pt?) in addition to signals for **4j,k,c,d** with relative intensities of *ca.* 12:2:3:1. Essentially pure samples of **4j** (5.6 mg) and **4k** (1.6 mg) were recovered by preparative TLC (dichloromethane/methanol, 39:1) from bands with R_f's of 0.6 and 0.5, respectively.

The reaction of **3d** (24 mg, 0.054 mmol) with **2c** (39 mg, 0.26 mmol) in $CDCl_3$ was monitored by ^{1}H and ^{31}P NMR spectroscopy, and consumption of the former was complete in 4 days. At this stage, the ^{31}P spectrum contained resonances for **4n,o** with relative intensities of *ca.* 3:1. Repeated preparative TLC (dichloromethane/methanol, 25:1, run twice; material from relevant bands replated) of this mixture gave an essentially pure sample of **4n** (17.7 mg) and a sample (4.8 mg) of **4o** containing some **3c** (*ca.* 20%). The former sample had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.74 (s, 3 H, COMe), 3.83 (d, J_{P-H} = 10.3 Hz, 6 H, POMe), 5.54 (m, J_{Pt-H} = 48 Hz, 2 H), 5.72 (m, J_{Pt-H} = 42 Hz, 1 H), 6.09 (m, J_{Pt-H} = 42 Hz, 1 H); the latter (**4o**) had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.69 (s, J_{Pt-H} = 4 Hz, 3 H, COMe), 3.77 (d, J_{P-H} = 10.7 Hz, 3 H, POMe), 3.83 (d, J_{P-H} = 10.7 Hz, 3 H, POMe), 4.87 (m, J_{Pt-H} = 47 Hz, 1 H), 5.62 (m, J_{Pt-H} = 44 Hz, 1 H), 5.77 (m, J_{Pt-H} = 44 Hz, 1 H), 6.14 (m, J_{Pt-H} = 44 Hz, 1 H).

Reaction of the Monoinsertion Products 3a–c with Methyl Diazoacetate (2d). The reaction of **3a** (11.5 mg, 0.030 mmol) with **2d** (40.0 mg, 0.40 mmol) in $CDCl_3$ (0.8 mL) was monitored by ^{1}H NMR spectroscopy. Resonances for **3a** were gradually replaced by those for **4i**, with *ca.* 10% conversion requiring 90 min and 85% conversion 18 h.

A sample of **3b** (46.0 mg, 0.10 mmol) in $CDCl_3$ (1.5 mL) was treated with **2d** (30.0 mg, 0.30 mmol). After 1 week at ambient temperature a ^{1}H NMR spectrum of the resulting solution was exceedingly complicated. It lacked resonances for **2d**, but signals for **3b** and a small proportion of **4i** were present. Preparative TLC (dichloromethane) of this mixture gave substrate (**3b**, 39.6 mg) and several small more polar fractions, one of which (3.5 mg) showed ^{1}H NMR resonances ascribable to **3d** and **4e,f**.

The reaction of **3c** (15 mg, 0.030 mmol) with **2d** (15 mg, 0.15 mmol) in $CDCl_3$ was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 6 days the ^{1}H NMR spectrum contained resonances for **2d** (*ca.* 20% of original intensity) and **3c** (<20%), while the ^{31}P NMR spectrum contained resonances for **4n,o**, **3c**, and **6e–h** in an approximate ratio of 50:50:20:4:2:1:1. Preparative TLC (dichloromethane/methanol, 24:1) gave two major fractions, the more polar (7.4 mg) of which contained mainly **4o** along with a smaller amount (*ca.* 30%) of **3c**, while the less polar (4.8 mg) was essentially pure **4n**.

Reaction of 1,2-Bis(diphenylphosphino)ethane (DPPE) with 3d and 4e,f. Samples (15.0 mg, 0.029 mmol) of both diesters were dissolved, separately, in $CDCl_3$ (0.75 mL), and DPPE (12.0 mg, 0.030 mmol) was added to each. ^{1}H NMR spectroscopy showed that the diene ligand was replaced by the phosphine in 3 h. The products **10b** (from **4e**) and **10c** (from **4f**) were purified by preparative TLC (dichloromethane/methanol, 49:1; on silica, **4e** is less polar than **4f**, but **10b** is more polar than **10c**). Diesters **10b,c** had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.39 (s, 6 H, Me) and 3.38 (s, 6 H, Me), respectively.

A solution of DPPE (28.3 mg, 0.071 mmol) in benzene (1 mL) was added to a solution of the monoester **3d** (31.7 mg, 0.071 mmol) in the same solvent (0.5 mL). A small amount (<1 mg) of a white solid precipitated immediately. After 4 h the solvent was evaporated and a ^{1}H NMR spectrum run on the residue. This showed only peaks for **10a**, free cyclooctadiene, and a trace of the substrate, **3d**. Preparative TLC (dichloromethane/methanol, 49:1, run twice) of the mixture gave pure **10a** (46.8 mg), which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.55 (s, 3 H, Me). DPPE (25.3 mg, 0.064 mmol) was dissolved, with stirring, in a solution of **10a** (46.8 mg, 0.064 mmol) in $CDCl_3$ (1 mL). Immediate darkening of the solution occurred, and white $[(DPPE)_2Pt]Cl_2$ crystallized rapidly. This solid was filtered off and showed a single ^{31}P resonance ($CDCl_3/CH_3OH$) at δ 47.6 ($^1J_{Pt-P}$ = 2330 Hz). A ^{1}H NMR (200 MHz) spectrum run on the filtrate showed, apart from some aromatic signals, mainly four resonances: δ 7.24 (residual proton resonance in solvent greatly enhanced), 4.056 (s, $ClCH_2CO_2Me$), 4.041 (t, $^2J_{D-H}$ = 2.2 Hz, $ClCDHCO_2Me$), and 3.78 (s, Me's). Integration showed that the ratio of $ClCDHCO_2Me$ to $ClCH_2CO_2Me$ was *ca.* 8:1. A ^{2}H NMR spectrum (61.395 MHz) of this solution contained resonances at δ 5.26 (s, CD_2Cl_2) and 4.04 (d, $^2J_{H-D}$ = 2.2 Hz, $ClCDHCO_2Me$), with an integrated ratio for CD_2Cl_2 to $ClCDHCO_2Me$ of 1:6.

DPPE (30.0 mg, 0.075 mmol) was dissolved, with stirring, in a solution of **3d** (30.0 mg, 0.067 mmol) in $CDCl_3$ (1 mL). Crystalline $[(DPPE)_2Pt]Cl_2$ started to precipitate immediately. After 50 min this solid (23.6 mg) was filtered off and a ^{1}H NMR spectrum run on the filtrate. This contained some aromatic signals and resonances for substantial amounts of **3d**, free cyclooctadiene, and $ClCDHCO_2Me$ and for smaller amounts of $ClCH_2CO_2Me$ and **10a**. More white solid precipitated when a further quantity (30.0 mg, 0.075 mmol) of DPPE was dissolved in this solution. When this solid (25.3 mg) was removed, a ^{1}H NMR spectrum of the resulting solution was very similar to that obtained, as above, from **10a** except for the presence of signals from free cyclooctadiene in the former.

Reactions of (*R,R*)-chiraphos with 3d and 4e,f. A sample of **3d** (259.5 mg, 0.582 mmol) was dissolved in warm benzene (5 mL) and the resulting solution placed under nitrogen after three freeze–pump–thaw cycles. The solution was then refrozen and

(*R,R*)-chiraphos (352.4 mg, 0.8263 mmol) added rapidly as the solid under nitrogen. The vessel was placed under vacuum and then refilled with nitrogen and warmed to ambient temperature. After 20 h, the walls of the vessel were washed down with benzene (5 mL, under nitrogen) and the resulting suspension was warmed at 60 °C for 4 h. After a further 16 h at ambient temperature a white solid had settled out, leaving a pale yellow supernatant. The residue remaining after removal of the solvent was subjected to preparative TLC (dichloromethane/methanol, run thrice, solvent ratios successively 197:3, 49:1, 39:1), which showed two major, close-running bands. These gave white solids, the less polar fraction (157.0 mg) consisting (^{1}H NMR spectroscopy) mainly of **5b** along with a minor amount (<2%) of **5c**, while the other fraction (226.7 mg) contained mainly **5c** and a lesser amount (<5%) of **5b**. These solids were purified by crystallization, the former from dichloromethane/benzene and the latter from benzene alone. The less polar fraction gave very small, colorless crystals consisting (^{1}H NMR spectroscopy) of essentially pure chloro[(*R*)-chloro(methoxycarbonyl)methyl][(2*R*,3*R*)-bis(diphenylphosphino)butane]platinum(II) (**5b**) with a small amount of dichloromethane and a trace of benzene retained in the crystals, even after drying *in vacuo*. These crystals had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.98 (m, 6 H, CMe's), 1.95 (m, 1 H, PCH), 2.34 (m, 1 H, PCH), 3.42 (s, 3 H, OMe), 7.49 (m, 8 H), 7.57 (m, 4 H), 7.70 (m, 2 H), 7.73 (m, 2 H), 7.83 (m, 2 H), 7.98 (m, 2 H). Anal. Calcd for $C_{31}H_{32}Cl_2O_2P_2Pt \cdot 0.02CH_2Cl_2$: C, 48.01; H, 4.19. Found: C, 48.03; H, 3.92. The more polar fraction gave long colorless needles consisting of fairly pure chloro[(*S*)-chloro(methoxycarbonyl)-methyl][(2*R*,3*R*)-bis(diphenylphosphino)butane]platinum(II) (**5c**) contaminated with *ca.* 1.5% of **5b** and benzene of crystallization. These crystals had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.03 (m, 6 H, CMe's), 1.96 (m, 1 H, PCH), 2.32 (m, 1 H, PCH), 3.48 (s, 3 H, OMe), 7.47 (m, 4 H), 7.51 (m, 4 H), 7.55 (m, 2 H), 7.57 (m, 2 H), 7.61 (m, 2 H), 7.63 (m, 2 H), 7.90 (m, 2 H), 8.06 (m, 2 H). Anal. Calcd for $C_{31}H_{32}Cl_2O_2P_2Pt \cdot 0.015C_6H_6$: C, 49.35; H, 4.27. Found: C, 49.37; H, 3.82.

A solution of diester **4e** (23.3 mg, 0.045 mmol) in $CDCl_3$ (0.2 mL) was degassed, as above for **3d** and chiraphos (23.0 mg, 0.054 mmol) was added under nitrogen. After 3 days, a further amount (0.6 mL) of $CDCl_3$ was added and ^{1}H and ^{31}P NMR spectra were run. The latter showed that *ca.* 40% of the chiraphos remained and that the major products were [{(*R,R*)-chiraphos}$_2$Pt]Cl_2 and **5d,e,b,c** in an approximate ratio of 8:4:3:2:2. The major product showed a ^{31}P resonance at δ 45.7 ($^1J_{Pt-P}$ = 2294 Hz). Peaks for **5f** were not visible in either spectrum. The solution was left at room temperature, under nitrogen, for a further 8 days, and the resulting product mixture was then submitted to preparative TLC (dichloromethane/methanol, 99:1). The three most polar bands, containing most of the material recovered, gave the following fractions, which are dealt with in decreasing order of polarity: (a) a fraction (18.9 mg) consisting largely of [{(*R,R*)-chiraphos}$_2$Pt]Cl_2; (b) essentially pure **5e** (5.7 mg) which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95 (m, 6 H, CMe's), 1.57 (m, 1 H, PCH), 1.94 (m, 1 H, PCH), 3.25 (s, 6 H, OMe's), 7.53 (m, 16 H), 8.03 (m, 4 H); (c) a fraction (6.8 mg) consisting largely of **5d**, along with a minor amount of **5c**. This fraction had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.96 (m, 6 H, CMe's), 1.57 (m, 1 H, PCH), 1.94 (m, 1 H, PCH), 3.22 (s, 6 H, OMe's), 7.50 (m, 8 H), 7.59 (m, 8 H), 8.06 (m, 4 H).

Diester **4f** (16.0 mg, 0.031 mmol) was treated with chiraphos (15.8 mg, 0.037 mmol) in the manner described immediately above. A ^{31}P NMR spectrum of the solution after 3 days showed that *ca.* 10% of the chiraphos remained, the major products being [{(*R,R*)-chiraphos}$_2$Pt]Cl_2 and **5f,c,b** in an approximate ratio of 14:4:2:1. Peaks for **5d,e** were not visible in this or a ^{1}H spectrum. Afer 8 days, the reaction mixture was separated by preparative TLC (dichloromethane/methanol, 197:3) and gave three major bands. The most polar one (12.5 mg) contained mainly [{(*R,R*)-chiraphos}$_2$Pt]Cl_2. A fraction (2.1 mg) of intermediate polarity consisted largely of **5c**. The third fraction (3.2 mg) contained mainly **5f**, along with a minor amount of **5b**, and had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.89 (m, 3 H, CMe), 1.00 (m, 3 H, CMe), 1.57 (m, 1 H, PCH), 1.93 (m, 1 H, PCH), 3.08 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 7.55 (m, 16 H), 8.02 (m, 4 H).

Reactions of [{(*R,R*)-chiraphos}PtCl$_2$] (5a) with 2b–d. Methyl diazoacetate (40.0 mg, 0.40 mmol) was added to **5a** (35.4 mg, 0.051 mmol) in dichloromethane (20 mL) and the resulting solution left in a refrigerator for 3 days. The solvent was evaporated *in vacuo* and a ^{31}P NMR spectrum of the residue run in $CDCl_3$. This contained resonances for **5a–c** in an approximate ratio of 5:3:2. The reaction residue was redissolved in dichloromethane (2 mL), and a further amount (44.5 mg, 0.45 mmol) of **2d** was added. After 3 days at room temperature, TLC (dichloromethane/methanol, 97:3) of the product still showed a spot corresponding to **5a** and more **2d** (45 mg) was added to the reaction mixture. After 4 days, a ^{31}P NMR spectrum of the reaction mixture contained resonances for major amounts of the platinalactone **9a** and of **5b**, smaller amounts of **5c** and three further platinalactones (**9b–d**), and traces of all three diesters **5d–f**. More **2d** (45 mg) was added to a solution of this mixture in dichloromethane (2 mL). After 7 days, resonances for **5b,c** were not visible in a ^{31}P NMR spectrum of the resulting product mixture. Preparative TLC (dichloromethane/methanol, 49:1) gave six substantial bands, only two of which contained (^{1}H NMR spectroscopy) appreciable amounts of Pt-containing compounds. A fraction (4.0 mg) with R_f 0.6 consisted mainly of **5f** along with some **5b**. The major fraction (24.7 mg) of R_f 0.2 contained the platinalactones **9a–d** and had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.94 (s, OMe, **9c**), 3.01 (s, OMe, **9a**), 3.04 (s, OMe, **9b**), 3.10 (s, OMe, **9d**) (ratio **9a:9b:9c:9d** *ca.* 5:1:1:1). This fraction was resubmitted to preparative TLC (dichloromethane/methanol, 197:3, run thrice) and the resulting band (R_f 0.45) divided into head, middle, and tail fractions. The three fractions all contained (^{31}P NMR spectroscopy) all four lactones, the least polar fraction being somewhat enriched, relatively, in **9a** at the expense of the most polar one.

(Trimethylsilyl)diazomethane in hexane (0.1 mL, 0.2 mmol) was added to a solution of **5a** (34.6 mg, 0.050 mmol) in dichloromethane (8 mL). After 3 days at ambient temperature, TLC (dichloromethane) showed a spot corresponding to substrate **5a**. More **2b** in hexane (0.1 mL, 0.2 mmol) was added and the reaction mixture left for an additional 2 days. TLC now showed a very weak spot corresponding to **5a**, and ^{1}H and ^{31}P NMR spectra were run on the product mixture. These contained resonances for **5g,h** in an approximate ratio of 5:1. Upon preparative TLC (dichloromethane, run twice) this mixture gave two major bands. The more polar one contained **5a** (7.0 mg) and the less polar, very narrow one (15.7 mg) mainly a mixture of **5g,h** which had ^{1}H NMR ($CDCl_3$, 200 MHz) δ –0.16 (s, SiMe, **5g**), –0.15 (s, SiMe, **5h**). (Trimethylsilyl)diazomethane in hexane (0.2 mL, 0.4 mmol) was added to **5a** (24.0 mg, 0.035 mmol) in dichloromethane (6 mL) and the resulting solution kept at 4 °C for 3 days. A ^{31}P NMR spectrum of the product mixture contained strong resonances for **5g** and weaker ones for **5h** (ratio *ca.* 20:1) and **5a**.

The diazophosphonate **2c** (45.0 mg, 0.30 mmol) was added to a solution of **5a** (34.6 mg, 0.050 mmol) in dichloromethane (8 mL). After 3 days, ^{1}H and ^{31}P NMR spectra of the product mixture contained resonances for **5i,j** in the approximate ratio of 5:1. Preparative TLC (dichloromethane/methanol, 37:3, run twice) gave several weak bands and one broad band, which was cut in three, a head, a middle, and a tail. The material recovered from all three sections contained mainly **5i** and a minor amount of **5j**. The most polar fraction (1.2 mg) and the middle fraction (4.6 mg) were contaminated with small amounts of dimethyl methylphosphonate; the least polar one (3.9 mg) was relatively clean. It had ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.31 (d, J_{P-H} = 10.6 Hz, OMe, **5i**), 3.48 (d, J_{P-H} = 10.5 Hz, OMe, **5j**), 3.58 (d, J_{P-H} = 10.3 Hz, OMe, **5i**), 3.61 (d, J_{P-H} = 10.5 Hz, OMe, **5j**). A reaction similar to the immediately preceding one was allowed to proceed for 7 days, this time at 4 °C. ^{1}H and ^{31}P NMR spectra showed the presence of **5i,j** in an approximate ratio of 8:1.

Reaction of (*R,R*)-chiraphos with 8a. A solution of the platinalactone **8a** (14.0 mg, 0.030 mmol) in $CDCl_3$ (0.2 mL) was

degassed, as above for **3d**, and chiraphos (23.0 mg, 0.035 mmol) was added under nitrogen. After 3 days at ambient temperature more $CDCl_3$ (0.6 mL) was added and ^1H and ^{31}P NMR spectra were run. These showed that essentially all of the cyclooctadiene ligand had been displaced by the phosphine to give mainly a mixture of **9a–d** (approximate ratio of 4:1:4:1) plus a substantial amount of $[\{(R,R)\text{-chiraphos}\}_2Pt]Cl_2$. Preparative TLC (dichloromethane/methanol, 197:3, run thrice) of this material gave a very polar material (8.6 mg) and a single, substantial band which contained **9a–d** (12.8 mg) in an approximate ratio of 9:6:3:2.

Reactions of the Monoesters 5b,c with Methyl Diazoacetate (2d). The following four solutions were made up in the indicated solvents (0.75 mL): (a) **5b** (11.5 mg, 0.015 mmol) plus **2d** (11.5 mg, 0.115 mmol) in $CDCl_3$; (b) **5b** (16.2 mg, 0.021 mmol) plus **2d** (19.1 mg, 0.191 mmol) in C_6D_6/dichloromethane (1:1); (c) **5c** (15.0 mg, 0.020 mmol) plus **2d** (15.2 mg, 0.152 mmol) in $CDCl_3$; (d) **5c** (16.2 mg, 0.021 mmol) plus **2d** (16.0 mg, 0.160 mmol) in C_6D_6/dichloromethane (1:1). The progress of the resulting reactions was monitored by ^{31}P NMR spectroscopy. After 18 h, the following extent of reaction was estimated from peak intensities: (a) 3–5%; (b) 1–2%; (c) 25–30%; (d) 3–5%. Essentially complete reaction was achieved in 6 days for (c) and 16 days for (d): after 16 days (a) was over 95% and (b) was about 60% complete. In both solvents, **5b** gave mainly **9a**, smaller amounts of **9b,c**, and even smaller quantities of **9d** and **5d,f**: **5c** gave mainly **9a**, some **9d**, smaller amounts of **9b,c** and **5e**, and a trace of **5f**.

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