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Characterization of the Intermediates in the Hydroformylation Reaction Catalyzed by Platinum Diphenylphosphinous Acid Complexes

Piet W. N. M. van Leeuwen,* Cornelis F. Roobeek, and John H. G. Frijns

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Postbus 3003, 1003 AA Amsterdam, The Netherlands

A. Guy Orpen

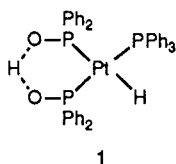
Department of Inorganic Chemistry, The University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

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This report describes the reactivity of compounds of the type $(\text{Ph}_2\text{POHOPPh}_2)\text{PtHL}$ (**1**), in particular the reactions related to hydroformylation. Ligands L carrying alkenyl and alkynyl groups ($\text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2$, $\text{Ph}_2\text{PCH}=\text{CH}_2$, $\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)_3$, $\text{Ph}_2\text{POC}_2\text{H}_4\text{CH}=\text{CH}_2$, $\text{Ph}_2\text{POC}_2\text{H}_4\text{C}\equiv\text{CH}$) undergo intramolecular insertion into the adjacent platinum-hydride bond. Diphenylvinylphosphine initially gives a phosphaplatinacyclopropane, which rearranges to $(\text{Ph}_2\text{POHOPPh}_2)\text{PtPh}_2\text{PCH}_2\text{CH}_2$ (**10**), a phosphaplatinacyclobutane complex for which the crystal structure has been determined ($\text{C}_{38}\text{H}_{35}\text{O}_2\text{P}_3\text{Pt}$, space group $P2_1/c$, $Z = 4$, $a = 10.622$ (2) Å, $b = 13.217$ (3) Å, $c = 24.563$ (5) Å, $\beta = 96.66$ (2)°). Alkene insertion can take place via a five-coordinate species, whereas the insertion of carbon monoxide seems to require a four-coordinate species with carbon monoxide as one of the ligands in the square plane. Prolonged hydroformylation with **1** gives rise to the formation of inactive complexes, which are shown to be dimeric platinum complexes containing a phosphido and a hydrido bridge. The crystal structure of one of these dimers has been determined, $\{(\text{Ph}_2\text{POHOPPh}_2)\text{Pt}\}_2(\mu\text{-PPh}_2)(\mu\text{-H})$ (**17a**; $\text{C}_{60}\text{H}_{53}\text{O}_4\text{P}_5\text{Pt}_2\text{C}_7\text{H}_8$, space group $P2_1/n$, $Z = 4$, $a = 15.745$ (3) Å, $b = 15.151$ (2) Å, $c = 25.677$ (5) Å, $\beta = 99.43$ (2)°). Surprisingly, the phosphido anion stems from diphenylphosphinous acid via reduction with acylplatinum complexes and not from triphenylphosphine.

Introduction

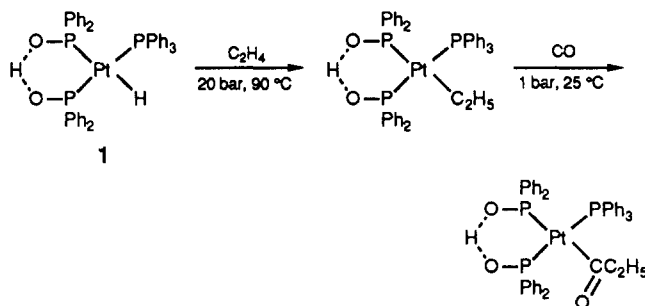
Since 1975 platinum complexes have been known as catalysts for the hydroformylation of terminal alkenes, giving highly linear aldehydes as the product.^{1,2} The presence of a trichlorostannate ion as one of the ligands has been considered a prerequisite for the complexes to be active catalysts. The actual role of SnCl_3^- has been the subject of many studies, and it has been questioned whether indeed it functions as a ligand.³ Cationic platinum complexes⁴ are active catalysts in the absence of SnCl_3^- , lending support to its role as a noncoordinating anion rather than as a ligand. We have reported⁵ on the catalytic activity of platinum complexes containing diphenylphosphinous acid as the ligand: complex **1**, earlier



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prepared by Roundhill et al.,⁶ catalyzes the hydrogenation of alkenes and the hydroformylation of terminal and in-

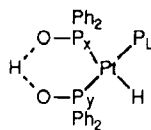
ternal alkenes. Both terminal and internal alkenes have a high preference for carbonylation at the terminal carbon atom, which leads to mostly linear oxo products (>90% and 70%, respectively). The aldehydes formed are in part hydrogenated to the corresponding alcohols. Diphenylphosphinous acid renders platinum catalytically active for a range of insertion reactions not found for any other platinum/ligand combination; only SnCl_3^- shows in part the same features. In addition to the catalytic reaction complex **1** was shown to undergo a stepwise hydroformylation reaction, as exemplified by the identification of the intermediate alkyl and acyl complexes:



This is peculiar because often the intermediates of a catalytic process escape isolation and identification. Still, several details evaded our direct observation, such as the interaction of the metal center with the alkene and carbon monoxide. Aiming to gain more insight into such interactions, we have now studied the reaction of platinum diphenylphosphinous acid complexes with alkenylphosphines.

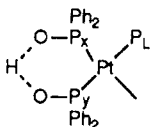
Initially one of the reasons for our choosing diphenylphosphinous acid (and its anion) as the ligand was its presumed stability under the conditions of a hydroformylation reaction. It is well-known that triaryl-

- (1) Schwager, I.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256.
- (2) Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553.
- (3) (a) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 427; *Organometallics* **1982**, *1*, 64. (b) Ruegg, H. J.; Pregosin, P. S.; Scriveranti, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* **1986**, *316*, 233. (c) Albinati, A.; Von Guten, U.; Pregosin, P. S.; Ruegg, H. J. *J. Organomet. Chem.* **1985**, *295*, 239. (d) Scriveranti, A.; Berton, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* **1986**, *314*, 369.
- (4) (a) Tang, S.; Kim, L. *J. Mol. Catal.* **1982**, *14*, 231. (b) Mrowca, J. U.S. Pat. Appl. 3876672, 1975.
- (5) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Wife, R. L.; Frijns, J. H. G. *J. Chem. Soc., Chem. Commun.* **1986**, 31.
- (6) Beaulieu, W. B.; Rauchfuss, T. B.; Roundhill, D. M. *Inorg. Chem.* **1975**, *14*, 1732.

Table I. ^{31}P NMR Data for Hydride Complexes^a 1-7

complex no.	P_L	δ			J					
		P_L	P_x	P_y	Pt- P_L	Pt- P_x	Pt- P_y	P_L - P_x	P_L - P_y	P_x - P_y
1	PPh_3	23.2	93.0	76.4	2242	2385	2960	17	367	29
3	$\text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2$	15.5	93.5	78.4	2221	2329	2916	15.5	367	28
4	$\text{Ph}_2\text{PCH}=\text{CH}_2$	14.5	91.5	77.8	2227	2328	2950	16.5	365	28.2
5	$\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)_3$	0.5	90.7	79.6	2164	2308	2872	19	373	29
6	$\text{Ph}_2\text{POC}_2\text{H}_4\text{CH}=\text{CH}_2$	112.6	91.4	79.2	2700	2296	2740	20	420	29
7	$\text{Ph}_2\text{POC}_2\text{H}_4\text{C}\equiv\text{CH}$	116.5	92.5	80.1	2700	2300	2751	20	428	30

^aChemical shifts in ppm relative to phosphoric acid; coupling constants in Hz.

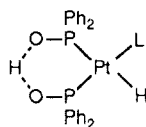
Table II. ^{31}P NMR Data for 8-16, 18, and 19

complex no.	δ , ppm			J , Hz					
	P_L	P_x	P_y	Pt- P_L	Pt- P_x	Pt- P_y	P_L - P_x	P_L - P_y	P_x - P_y
8	51.6	88.7	79.7	2432	2072	3161	16.5	383	32
9	-15.8	92.0	80.4	1420	3099	3692	24.5	323	26
10	-70.4	89.2	71.4	1584	2116	3204	5	418	28
11	40.7	87.1	80.3	2370	2040	3056	16	385	33
12	99.9	87.9	80.1	2956	1889	3007	13.3	422	35.4
13a	101.2	84.6	73.3	2570	2140	2970	16	418	32
13b	137.0	87.3	81.4	2940	2315	3124	4.6	409	33
14	144.4	86.0	80.2	2830	2077	3070	8	399	35.8
15	48.1	80.6	76.3	2560	1850	3378	17.2	380	38.2
16	105.5	79.3	62.6	2970	1746	2945	16	366	40
18	105.8	87.7	62.2	3065	1741	3080	30.4	401	36
19	106.0	88.1	63.1	3068	1718	3077	30.6	403	36.2

phosphines may undergo a phosphorus-to-carbon bond cleavage reaction under such reducing conditions.⁷ We observed, however, that phosphinites also lack stability in prolonged reactions. Here we report on the reaction leading to the deactivation of the platinum catalyst and the structure of the bimetallic compound formed.

Results and Discussion

Insertion Reactions of Alkenylphosphines. Complexes 3-7 are obtained by treatment of 1 or 2 with the appropriate phosphine. Compound 2 is prepared from



- 2, L = Ph_2POH
- 3, L = $\text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2$
- 4, L = $\text{Ph}_2\text{PCH}=\text{CH}_2$
- 5, L = $\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)_3$
- 6, L = $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{CH}=\text{CH}_2$
- 7, L = $\text{Ph}_2\text{POCH}_2\text{CH}_2\text{C}\equiv\text{CH}$

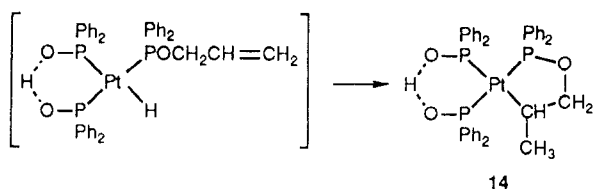
$\text{Pt}(\text{PPh}_3)_4$ and diphenylphosphinous acid: it is insoluble in dichloromethane and acetone, and its structure is not known. It can be described as an analogue of hydride 1 or, alternatively, as platinum tris(diphenylphosphinous acid), the empirical formula of the compound. The phosphines L used in the exchange reaction with 1 or 2

include alkenylphosphines, alkenylphosphinites, and an alkenylphosphinite. The complexes obtained have been characterized by their ^{31}P (Table I) and ^1H NMR spectra, which give sufficient proof for their structure, since the phosphorus chemical shift and the Pt-P and P-P coupling constants provide ample information in support of this (the chemical shift is indicative of the nature of the phosphorus ligand, the ligand coordinated trans to the phosphorus, and the occurrence of a ring structure; the platinum-phosphorus coupling constant provides a measure of the trans influence of the trans ligand; the P-P coupling constants show the mutual positions of the phosphorus ligands). From the data in Table I it is clear that in complexes 3-7 straightforward coordination via the phosphorus atom occurs and the spectra contain no signs of alkene-to-platinum interaction. For example, the spectrum of 3, with diphenylallylphosphine as the ligand, strongly resembles the spectrum of 1 with triphenylphosphine. The platinum coupling of P_x is characteristic of a compound with a hydride in the trans position. The allyl moiety shows no changes in proton NMR spectra that could point to interaction with the platinum center.

When the compounds are heated or allowed to stand, insertion of the alkene (3-6) and alkyne (7) into the platinum-hydrogen bond takes place, forming the cyclic phosphaplatina alkyls 8-12 and vinyl 13a (see Table II). Likewise, the allyl ester of diphenylphosphinous acid, for which no intermediate hydride was found, forms the insertion product 14. Vinylidiphenylphosphine gives two products: 9 and 10. The former is the initial product followed by kinetic control; the latter is the thermody-

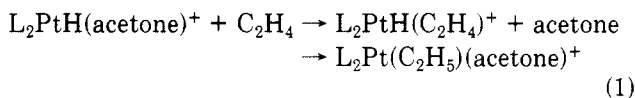
(7) Garrou, P. E. *Chem. Rev.* 1985, 85, 171.

phosphinous acid. No starting hydride was observed;



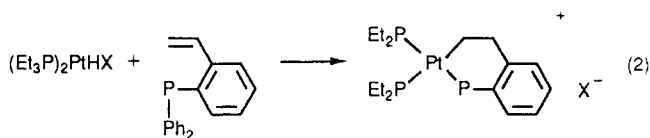
instead, the cyclic insertion product was formed immediately upon addition of the ligand. The low-field shift in 14, as in 13b, is typical of a five-membered ring.

Alkene Insertion. The alkene insertion itself deserves further comment. It is generally accepted that alkene insertion at platinum hydrides takes place in square-planar intermediates in which the alkene and hydride assume a cis position. There are indeed several cis complexes that undergo insertion, and there is at least one study¹¹ (eq 1)



showing the preference for square-planar intermediates relative to five-coordinated species. One exception has been reported¹² ($L_2PtHSnCl_3$), which is believed to be five-coordinated in the intermediate complex. Theoretical studies¹³ lend support to the preference for square-planar intermediates, with an added strong requirement for coplanarity of the Pt-H and C=C bonds.

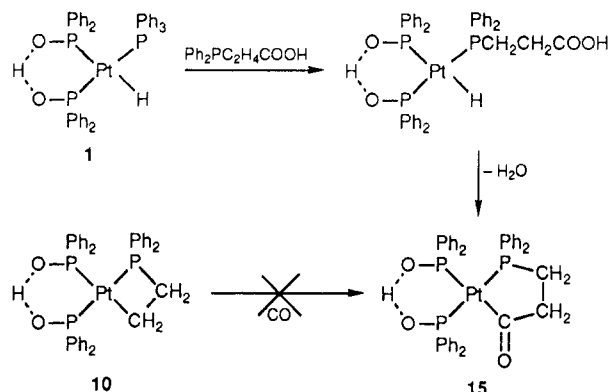
In the literature one example is known of an intramolecular insertion reaction resembling our results¹⁴ (eq 2).



The same *o*-styrylphosphine ligand is reported to undergo this reaction with Re and Mn hydrides.¹⁵ The authors do not comment on the detailed mechanism; they only speculate on phosphine coordination before insertion takes place. For the reverse reaction, i.e. β -elimination of alkenes from (di)alkylplatinum complexes, both three- and four-coordinate precursors have been proposed.¹⁶ In the latter case no phosphine dissociation occurs prior to β -elimination, and a five-coordinate product or intermediate has been postulated. In general the insertions observed here proceed more easily than the insertion of ethene into 1, which only occurs at higher temperatures (20 bar, 90 °C). For the insertion process a chelating effect should therefore be considered and five-coordinate intermediates may be involved.

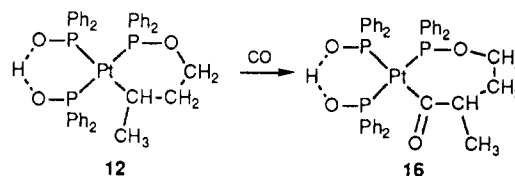
Insertion of Carbon Monoxide. In the catalytic hydroformylation of ethene with use of complex 1 the insertion of carbon monoxide was found to be a fast and reversible process. Much to our surprise complexes 8-14 (with the exception of 12) failed to undergo carbon monoxide insertion (40 bar, 85 °C). Hence, the chelating alkylphosphines prohibit the formation of functionalized

(aldehyde, alcohols, carboxylic acids) phosphines via this route. This is a kinetic and not a thermodynamic constraint, as appears from the proven stability of 15. Compound 15 cannot be obtained from 10 via insertion of carbon monoxide, but it was easily formed from 1:



The formation of acyl complex 15 via (diphenylphosphino)propionic acid involves the elimination of water. The alternative reaction giving dihydrogen and a carboxylate does not take place.

Complex 12 reacted with carbon monoxide (40 bar, 85 °C), giving the seven-membered ring compound 16, which shows that chelation does not prevent insertion in all cases.



The carbonylation of related platinum complexes of the type *cis*-[PtXRL₂] has been extensively studied.¹⁷ In general the carbonylation is slow in coordinatively saturated complexes. Both dissociative and associative¹⁸ pathways may be used to rationalize the results, with a preference for dissociative processes. The latter mechanism explains the inactivity shown by most of the present complexes.

In conclusion, the intramolecular insertion of alkenes into a Pt-H bond is a facile process in complexes 3-7 compared to the intermolecular insertion of ethene in the catalytic cycle of 1. On the other hand, carbon monoxide inserts only on one occasion into the chelating alkylplatinum bond. Insertion of CO in nonchelating alkyl complexes formed from 1 occurs readily⁵ at 1 bar and 25 °C. Coordination of carbon monoxide in the square plane may well be a prerequisite.

Hydrogenolysis of Platinum-Carbon Bonds. Mechanistically¹⁹ of great importance is the final step in the hydroformylation reaction cycle, viz. the reaction of the platinum acyl intermediate with dihydrogen or another hydrogen source. Previously⁵ we have pointed out that

(17) Anderson, G. K.; Lumetta, G. J. *Organometallics* 1985, 4, 1542.

(18) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* 1980, 1434.

(19) A reaction of the hydride complex and the acyl complex did not lead to the aldehyde. This reaction has been considered as a step in the hydroformylation of alkenes with cobalt carbonyl catalysts,^{19a-d} and a stoichiometric example with $Cp(CO)_2MoCOR$ and $Cp(CO)_2MoH$ has been reported.^{19e} (a) Alemdaroglu, N. H.; Penninger, J. L. M.; Oltay, E. *Monatsh. Chem.* 1976, 107, 1153. (b) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* 1985, 107, 666. (c) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* 1986, 5, 209. (d) Major, A.; Horváth, I. T.; Pino, P. *J. Mol. Catal.* 1988, 45, 275. (e) Jones, W. D.; Huggins, J. M.; Bergmann, R. G. *J. Am. Chem. Soc.* 1981, 103, 4415.

(11) Clark, H. C.; Jablonski, C. R. *Inorg. Chem.* 1974, 13, 2213.

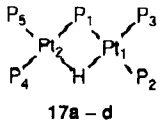
(12) Clark, H. C.; Jablonski, C. R.; Halpern, J.; Weil, T. A.; Mantovani, A. *Inorg. Chem.* 1974, 13, 1541.

(13) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 2079.

(14) Brookes, P. R. *J. Organomet. Chem.* 1973, 47, 179.

(15) Bennett, M. A.; Watt, R. *J. Chem. Soc. D* 1971, 94.

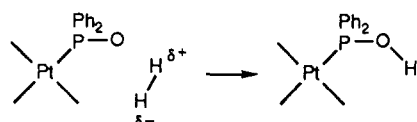
(16) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* 1982, 1, 1528.

Table III. ^{31}P NMR Data for Dimers 17a-d^a


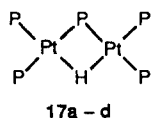
	17a ^b	17b	17c	17d ^c
$\delta(\text{P}_1)$	99.5	208	157.5	193
$\delta(\text{P}_2)$	79.5	120	81.5	127
$\delta(\text{P}_3)$	60	19	22	23
$\delta(\text{P}_4)$	79.5	120		124
$\delta(\text{P}_5)$	60	19		67
$J_{\text{P}_1-\text{P}_2}$	270	263	285	245
$J_{\text{P}_1-\text{P}_3}$	6	5	11	12 ^d
$J_{\text{P}_1-\text{P}_4}$	270	263	285	245
$J_{\text{P}_1-\text{P}_5}$	6	5	11	17
$J_{\text{P}_2-\text{P}_3}$	31	<5		25 ^d
$J_{\text{P}_3-\text{P}_5}$	48			122
$J_{\text{Pt}_1-\text{P}_1}$	1700	2535	2447	2470
$J_{\text{Pt}_1-\text{P}_2}$	2910	3520	3802	3850
$J_{\text{Pt}_1-\text{P}_3}$	3800	3410		3320
$J_{\text{Pt}_1-\text{P}_4}$	23	45		
$J_{\text{Pt}_1-\text{P}_5}$	210	255		210
$J_{\text{Pt}_2-\text{P}_1}$	1700	2535	2447	2595
$J_{\text{Pt}_2-\text{P}_2}$	23	45		65
$J_{\text{Pt}_2-\text{P}_3}$	210	255		135
$J_{\text{Pt}_2-\text{P}_4}$	2910	3520		3380
$J_{\text{Pt}_2-\text{P}_5}$	3800	3410		3850

^a δ values are in ppm and J values in Hz. ^b Proton NMR: $\delta = -5.58$; $J_{\text{Pt}-\text{H}} = 469$ (triplet), $J_{\text{P}_3-\text{H}} = 70$ (triplet), $J_{\text{P}_2-\text{H}} = 10$ (triplet), $J_{\text{P}_1-\text{H}} = 17$ Hz. ^c Additional values: $J_{\text{P}_2-\text{P}_4} = 15$, $J_{\text{P}_4-\text{P}_5} = 15$ Hz. ^d Values may be interchanged.

metal phosphinito complexes could be ideal for the heterolytic splitting of dihydrogen:

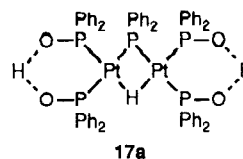


Ligand Decomposition under Hydroformylation Conditions. After hydroformylation of various alkenes for several hours with 1 as the catalyst the platinum compound was found to be present as the starting hydride 1 and the corresponding acyl complex. For ethene the two compounds were observed in roughly equal amounts, but more drastic evacuation during the isolation led to formation of pure 1. Prolonged hydroformylation (24 h) caused complete decomposition, and a very complex ^{31}P NMR spectrum was recorded, showing the presence of at least four species, all containing platinum dimers with a phosphido bridge. The results of the ^{31}P NMR analysis of compounds 17a-d are presented in Table III. The ratio in which the platinum dimers were formed during the decomposition reaction was not reproducible, and all but 17a were unstable during workup via column chromatography. Attempted isolations always resulted in 17a. The general formula for these complexes according to ^{31}P NMR spectroscopy is

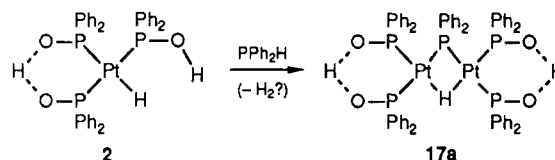


The bridging phosphido groups are observed between 100 and 220 ppm, and the four other phosphorus signals occur both in the phosphine resonance region and in the phosphinous acid resonance region. When the inactive catalyst solution was kept at room temperature for 3 days, yellow

crystals separated from the orange solution, being complex 17a. This complex was characterized by its proton and



phosphorus NMR spectra (Table III), and its structure was solved by an X-ray determination (vide infra). The ^{31}P phosphido resonance of 17a is observed at 99.5 ppm; it shows couplings with the trans-phosphinito groups of 270 Hz, while the couplings with the cis-phosphinito groups amount to 6 Hz. Furthermore, it exhibits the expected 1:8:18:8:1 multiplet due to coupling with two equivalent platinum nuclear spins. The proton NMR spectrum of 17a gives a hydride resonance at -5.58 ppm, consisting of 90 lines (which are all observed) due to a platinum multiplet (469 Hz), a phosphorus triplet (70 Hz, trans), a phosphorus doublet from the phosphido group (17 Hz), and a phosphorus triplet (10 Hz, due to the cis phosphorus atoms). It is worth mentioning that the $^1J_{\text{Pt}-\text{P}}$ coupling constant of the phosphorus trans to the bridging hydride is very large (3800 Hz), much larger than in compounds with a nonbridging hydride (~ 2300 Hz), indicating that the trans influence of a bridging hydride is much smaller and comparable with that of, for example, chloride. The σ -interaction of the bridging phosphido group with platinum is also small, as appears from its platinum coupling of only 1700 Hz. All NMR and structural data are consistent with what is to be expected. The independent synthesis of 17a from 2 and diphenylphosphine was successful.



For compounds 17b-d we propose essentially the same structure, with part of the diphenylphosphinous acid being replaced by another neutral ligand. Compound 17b is also a symmetric complex, and the two neutral ligands with a ^{31}P resonance at 19 ppm are PPh_3 . Complexes 17c and 17d are asymmetric and contain one PPh_3 and a second ligand, which is phosphinous acid and an organic phosphinite, respectively (vide infra). Although their structures have not been thoroughly proven, the NMR data of these compounds have been included in Table III for the sake of completeness, as they are always present in the crude reaction mixture leading to 17a.

The ^{31}P chemical shift of bridging phosphido ligands has been the subject of many discussions.²⁰⁻²⁴ Their resonance may be observed anywhere between -300 and $+400$ ppm. High-field values have been correlated with large M-P-M angles and low-field (positive) values with acute M-P-M angles.⁹ More recently the consensus has grown that

(20) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349.

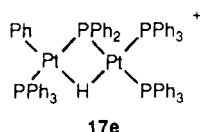
(21) Glaser, R.; Kountz, D. J.; Waid, R. D.; Galluci, J. C.; Meek, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 6324.

(22) Rosenberg, S.; Mahoney, W. S.; Hayes, J. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1065.

(23) Berry, D. E.; Bushnell, G. W.; Dixon, K. R.; Moroney, P. M.; Ch'eng Wan *Inorg. Chem.* **1985**, *24*, 2625.

(24) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 559.

low-field values are indicative of the presence of a metal-metal bond.²⁴ Exceptions to the empirical rules have been recorded.²⁴ Many species containing both a bridging phosphide and a bridging hydride have been reported. Homobimetallic complexes have been prepared for, inter alia, Mo,²⁵ Mn,²⁶ Fe,²⁷ and Pt.²⁸ More recently heterobimetallic complexes have received a great deal of attention.²⁹⁻³² All of these complexes have a low-field shift for the phosphido resonance in common. The bonding can be described as a two-electron-three-center bond. Alternatively, the structural unit in these complexes can be viewed as a protonated metal-to-metal bond.^{33,34} The structural unit of complexes **17a-d** closely resembles that of **17e** first reported by Jans et al.²⁸ The same cationic



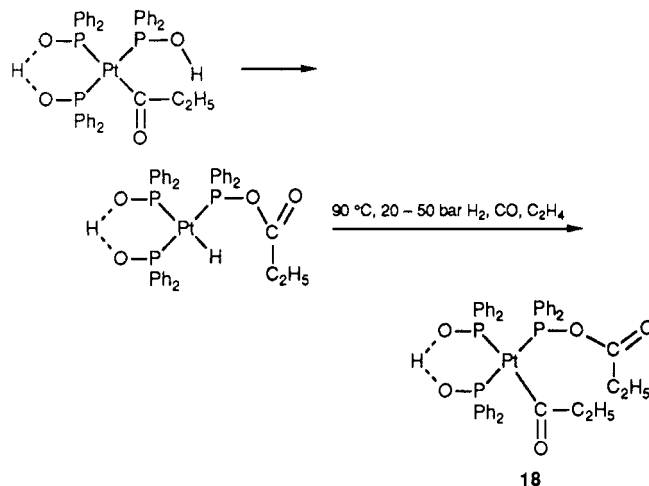
dimer has been reported³⁵ with $\text{CHC}(\text{SO}_2\text{CF}_3)_2^-$, a fluorocarbon acid, as the anion instead of BF_4^- . The ^{31}P NMR spectra of the phosphido bridges of **17a** and **17e** are strikingly similar, except for the lower symmetry of the latter. The coordinating phenyl group causes slight deviations. The $^1J_{\text{Pt-P}}$ coupling constants of triphenylphosphine and diphenylphosphinous acid are, as in most other complexes, of about the same magnitude.

Formation of Phosphido Species. Decomposition of triarylphosphine to phosphido species is a common reaction often encountered in catalytic reactions with phosphine complexes of noble metals.⁷ Complex **17e** cited above owes its phosphido bridge and its phenyl group to a splitting of triphenylphosphine.^{28,35} Under the conditions of a catalytic reaction where carbon monoxide, hydrogen, and ethene are present, the aryl group often end up in products such as benzene, benzaldehyde, benzyl alcohol, and ethylbenzene. The diphenylphosphide formed is a nuisance, since it complexes strongly to the metal and inactive complexes usually result. When the present reaction was run in toluene, none of the organic byproducts mentioned were found by GC analysis; instead, traces of propionic acid were found. Direct evidence that the phosphido anion does not originate from triphenylphosphine was obtained when in compound **1** the ligand triphenylphosphine was replaced by tri-*p*-tolylphosphine. After the hydroformylation reaction with ethene the usual mixture of **17a-d** was observed in ^{31}P NMR spectra. Workup of the resulting dark orange inactive solution gave **17a**, which according to ^1H NMR spectroscopy did not

contain any tolyl groups. Tritolylphosphine was recovered unchanged. Therefore, it is concluded that the diphenylphosphido anion originates from diphenylphosphinous acid ("diphenylphosphine oxide").

As mentioned, traces of propionic acid were also observed, both by GC and by ^1H NMR methods. Propionic acid and the phosphido fragment were formed in roughly equimolar amounts. Formation of propionic acid from ethene is hard to explain, as this would require the presence of water or oxidants. Repeated experiments with careful exclusion of water and oxygen and thorough analysis of the organic products proved that the only source of oxygen that could lead—with ethene, carbon monoxide, and hydrogen—to propionic acid was in fact diphenylphosphinous acid. This is very surprising, since the phosphine-oxygen double bond is extremely stable toward cleavage. ^1H NMR integration showed that after workup indeed roughly one propionic acid molecule was formed per molecule of platinum dimer. Hence, the formation of propionic acid and the absence of tolyl groups in the phosphido anion nicely prove that the latter stems from the phosphinous acid ligand.

More details of the mechanism have been obtained from another intermediate, **18**, which was observed in the catalytically active reaction mixtures just before dimer formation started. This was not quantitatively reproducible, and sometimes **17a-d** and **18** were formed simultaneously. Eventually **18** disappeared and only the dimeric complexes were observed. The formation and the structure of **18** can be depicted as



It is proposed that the acyl group formed at platinum during hydroformylation migrates to the oxygen of diphenylphosphinous acid, not necessarily via an intramolecular process. The new ligand formed is a mixed anhydride of propionic acid and phosphinous acid, and its instability during column chromatography is not unexpected. The mixed anhydride is also observed as one of the ligands in **17d**, which after chromatography gives **17a**. Complex **18** is smoothly converted under hydroformylation conditions but also under reflux with **1** or **2** in toluene into dimeric compounds **17**. This is not surprising, since a common method for the preparation of phosphido complexes involves reaction of $\text{Ph}_2\text{P}(\text{O}_2\text{CC}_2\text{H}_5)$ with reducing metal complexes; propionate can be removed in a similar process from $\text{Ph}_2\text{P}(\text{O}_2\text{CC}_2\text{H}_5)$. For comparison we have prepared **19**, containing ethyl phosphinite as the ligand. The ^{31}P NMR spectrum strongly resembles the spectrum of **18**, but proton NMR spectroscopy shows the expected differences; i.e., both the resonances of an acyl group and the resonances of an ethoxy group are observed. Compound **19**

(25) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031.

(26) Hayter, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 823.

(27) Hayter, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3120.

(28) Jans, J.; Naegeli, R.; Venanzi, L. M.; Albinati, A. *J. Organomet. Chem.* **1983**, *247*, C37.

(29) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *J. Chem. Soc., Chem. Commun.* **1985**, 1314.

(30) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987**, 1557.

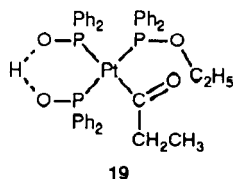
(31) Lin, J. T.; Hsiao, Y.-M.; Liu, L.-K.; Yeh, S. K. *Organometallics* **1988**, *7*, 2065.

(32) Powell, J.; Sawyer, J. F.; Shiralian, M. *Organometallics* **1989**, *8*, 577.

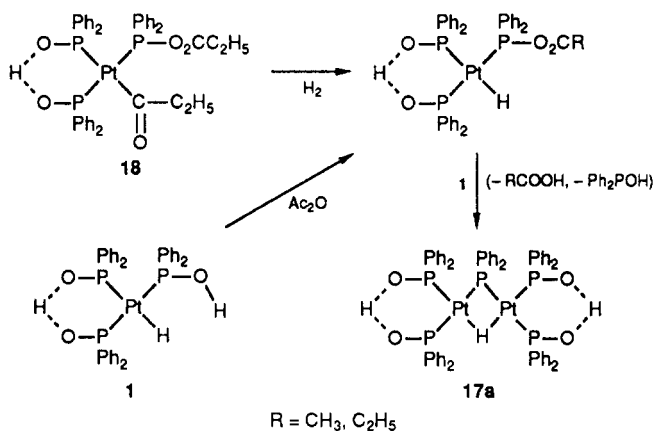
(33) Often the complexes are made in this way. Protonation of $[(\text{Cp})(\text{Co}(\mu\text{-PPh}_2))_2]$ leads to the bridged hydride complex and the ^{31}P resonance shifts to slightly lower field from 120 to 132 ppm. However, addition of SO_2 to the cobalt-cobalt bond leads to bond rupture and the phosphido resonance shifts upfield to -76 ppm. Chen, L.; Kountz, D. J.; Meek, D. W. *Organometallics* **1985**, *4*, 598.

(34) Werner, H.; Klingert, B.; Rheingold, A. L. *Organometallics* **1988**, *7*, 911.

(35) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767.



neither loses its ethoxy group to form phosphido complexes nor is it observed in the reaction mixture, so it can be ruled out as an intermediate in the formation of 17 or 18. An alternative way to form phosphinous acid propionic anhydride may be treatment of phosphinous acid with acetic anhydride. Indeed, addition of acetic anhydride to re-



fluxing 1 or 2 in toluene gives within 15 min the characteristic red color and ³¹P NMR spectra of the dimeric complexes; this points to the formation of 17 through the intermediacy of 18 or similar complexes.

The above results show that Pt(μ-H)(μ-PPh₂)Pt is a stable bonding unit that is preferentially formed under severe conditions. In addition, we have seen that diphenylphosphinous acid can be reduced by platinum acyl complexes. Eventually, via the complexed mixed anhydride, carboxylic acid and diplatinum phosphido-hydrido complexes are formed. This is quite unexpected and disappointing, since in view of the similarities of PPh₃ and Ph₂POH as ligands a high stability of the latter under hydroformylation conditions would have been very attractive.

Description of the Structure of (Ph₂POHOPPh₂)-Pt(Ph₂PCH₂CH₂) (10). The crystal structure of 10 consists of isolated molecules of 10 separated by normal contact distances. Figure 1 illustrates the geometry of the complex and shows the labeling scheme used. Figure 2 provides a view of the coordination geometry around the platinum atom approximately parallel to the coordination plane. Molecules of 10 contain a platinum atom chelated by Ph₂PCH₂CH₂ and Ph₂PO-H-OPPh₂ ligands. The platinum atom lies close to the least-squares plane through it and the four contact ligand atoms, as would be expected for the formal oxidation state of +II. Deviations from the plane are as follows (Å): Pt, 0.012; P(1), -0.031; P(2), 0.018; P(3), -0.028; C(1), 0.030; C(2), -0.501; O(2), 0.738; O(3), 0.300 Å. The small bite of the Ph₂PCH₂CH₂ ligand causes some distortion of the valence angles at platinum away from ideal square-planar values (e.g. P(1)-Pt-C(1) = 68.3 (2)°). It is notable that it is the angles involving the phosphorus of this ligand (P(1)) that are most readily distorted (e.g. P(1)-Pt-P(2) = 106.2 (1)°; cf. C(1)-Pt-P(3) = 94.4 (2)°; similar distortions are observed in [Re(CO)₄(Ph₂PCH₂CH₂)].³⁶ The geometry in the four-mem-

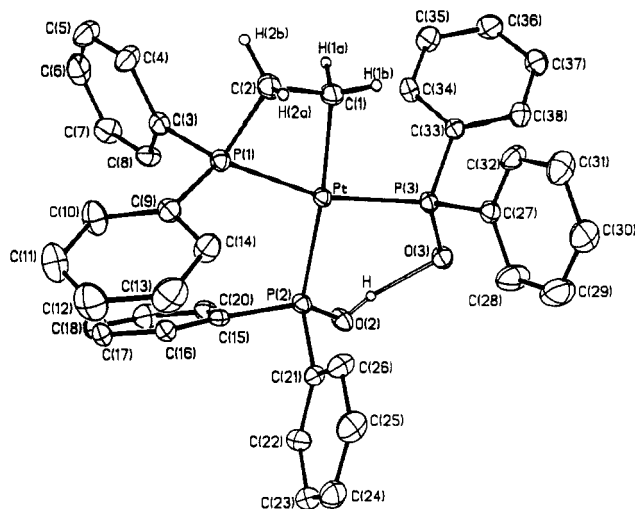


Figure 1. Molecular structure of 10 with atom labels. Hydrogen atoms of phenyl groups are omitted for clarity. Non-hydrogen atoms are drawn to enclose 50% probability density.

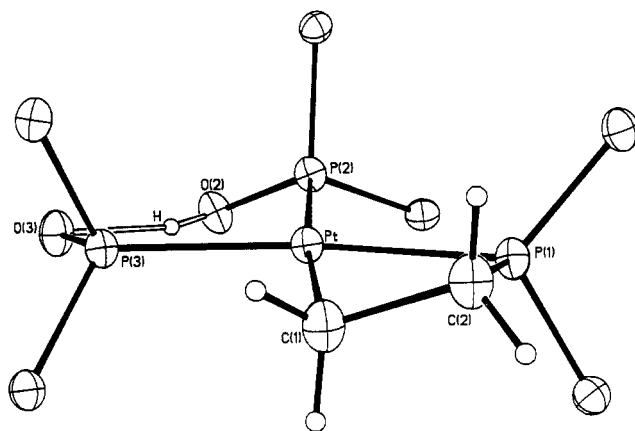


Figure 2. Coordination geometry of 10 with all phenyl group atoms omitted except ipso carbons. Non-hydrogen atoms are drawn to enclose 50% probability density.

bered ring Pt-P-C-C is indicative of considerable strain. Thus, the valence angles at phosphorus (88.1 (2)°), carbon (P(1)-C(2)-C(1) = 94.6 (2)° and Pt-C(1)-C(2) = 102.4 (4)°), and platinum are well below their usual values. The C-C length is rather long (1.573 (9) Å). The four-membered ring is puckered, showing intra-ring dihedral angles as follows: Pt-P(1)-C(2)-C(1) = 20.2°, P(1)-C(2)-C(1)-Pt = -22.7°, C(2)-C(1)-Pt-P(1) = 19.0°, C(1)-Pt-P(1)-C(2) = -15.9°.

In contrast, the diphenylphosphinite-diphenylphosphinous acid ligand chelates platinum to give a near-ideal valence angle at platinum, 91.1 (1)°. The Pt-P distances for this ligand show asymmetry presumably induced by the trans influence of the Ph₂PCH₂CH₂ group: Pt-P(2) = 2.305 (2) Å trans to C, Pt-P(1) = 2.288 (2) Å trans to P. These variations are in accord with the Pt-P coupling constants in Table II. The Pt-P distances are similar to those in 17a. The pseudo-five-membered (Pt-POOP) ring is not planar and, hence, shows intra-ring dihedral angles as follows: Pt-P(2)-O(2)...O(3) = 31.2°, P(2)-O(2)...O(3)-P(3) = -20.7°, O(2)...O(3)-P(3)-Pt = -0.3°, O(3)-P(3)-Pt-P(2) = 14.9°, P(3)-Pt-P(2)-O(2) = -30.9°. The O(2)...O(3) distance (2.476 (8) Å) is indicative of strong hydrogen bonding. Although the hydrogen of this O-H-O system is not reliably located, it seems to lie close to the O(2)...O(3) vector (O(2)-H-O(3) = 168 (5)°), and it is interesting to note that the asymmetry in O-H distances is mirrored by an asymmetry in P-O distances

(36) Lindner, E.; Funk, G.; Hoehne, S. *Chem. Ber.* 1981, 114, 2465.

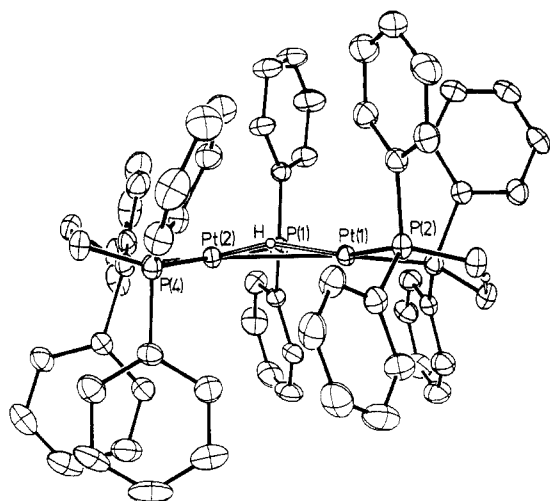


Figure 3. Molecular geometry of 17a. All phenyl group hydrogen atoms have been omitted for clarity. Non-hydrogen atoms are drawn to enclose 50% probability density.

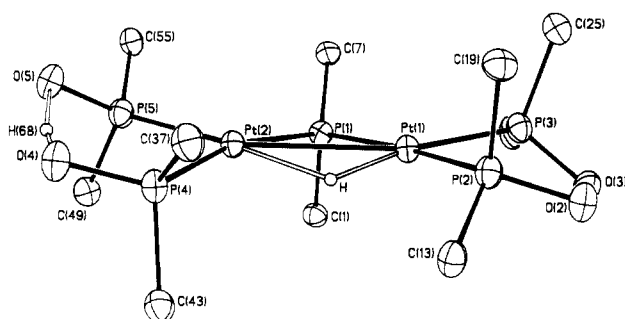


Figure 4. Coordination geometry around the two platinum atoms of 17a with all phenyl group atoms other than ipso carbons omitted for clarity. Non-hydrogen atoms are drawn to enclose 50% probability density.

(O(2)–H = 0.79 (8), P(2)–O(2) = 1.580 (5) Å; O(3)–H = 1.70 (8), P(3)–O(3) = 1.537 (4) Å).

Description of the Structure of Dimer 17a. The crystal structure of 17a as its toluene solvate consists of isolated molecules of the complex and the solvent. Figure 3 illustrates the geometry of the complex, and Figure 4 shows the labeling of the atoms used. Molecules of 17a contain a dimeric platinum unit bridged by hydride and μ -diphenylphosphido ligands, each platinum being chelated by a $\text{Ph}_2\text{PO-H-OPPh}_2$ moiety. The coordination geometry about each platinum is approximately square planar, as is appropriate for formal oxidation state +II for each platinum. Deviations of the ligands around platinum from the least-squares PtP_3 planes are small for Pt(1) and larger for Pt(2) (Pt(1) distances in Å P(1) 0.002, P(2) 0.002, P(3) 0.000, Pt(1) –0.004, Pt(2) –0.282, H 0.19; Pt(2) distances in Å P(1) 0.049, P(4) 0.047, P(5) 0.011, Pt(2) –0.108, Pt(1) –0.474, H –0.11; estimated standard deviations ca. 0.002, 0.004, and 0.07 Å for Pt, P, and H, respectively), indicating a twisting of the coordination “plane” of Pt(2). The coordination least-squares planes are inclined at an angle of 14.3° to one another, as may be seen in Figure 4. The Pt– PPh_2 distances show a pronounced variation, in a manner consistent with the Pt–P coupling constants of Table III. The Pt–P distances trans to μ - PPh_2 are longer than those trans to μ -H: Pt(1)–P(2) = 2.318 (2), Pt(2)–P(4) = 2.333 (2) Å vs Pt(1)–P(3) = 2.275 (2) Å Pt(2)–P(5) = 2.279(2) Å. The coordination of the μ - PPh_2 ligand is near-symmetric (Pt(1)–P(1) = 2.295 (2), Pt(2)–P(1) = 2.308 (2) Å) and shows an acute Pt–P–Pt angle of $78.3 (1)^\circ$, as required by the short Pt–Pt distance. If the μ -phosphido

ligand is assumed to be a four-electron anionic donor and the μ -hydride ligand is treated as a two-electron anionic donor, the total valence electron count around the two metals sums up to 30 electrons. This implies a three-center–two-electron bond for Pt–H–Pt, which is consistent with the platinum–platinum distance of 2.907 (1) Å. The closest structural resemblance to 17a is displayed by $[\text{Pt}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{PPh}_3)_3(\text{Ph})]\text{BF}_4^{28}$ (17e), which shows Pt–Pt distances of 2.89 and 2.91 Å for two independent molecules in the unit cell. These distances are significantly longer than those in Pt(I) complexes with a Pt–Pt metal–metal single bond, as in $(\mu\text{-dpm})_2\text{Pt}_2\text{Cl}_2$,³⁷ in which the distances³⁸ are around 2.60 Å. When the Pt(I) complexes are oxidized with formation of Pt(II) *A-frame* complexes, the platinum-to-platinum distance is increased³⁸ to values in the range of 2.9–3.2 Å as in the μ -hydride complex $(\text{dpm})_2(\text{Pt})_2(\mu\text{-H})(\text{CH}_3)_2^+$ (2.93 Å),³⁹ i.e. the same as in compounds 17a and 17e. The μ -phosphido ligand, which bridges the two-electron–three-center bond in 17a, shows a low-field ^{31}P NMR shift, as is observed for all complexes containing this structural unit.

The hydride ligand is located by the X-ray diffraction data, but not very accurately, giving Pt–H distances of 1.94 (7) and 1.65 (6) Å, with a Pt(1)–H–Pt(2) angle of $108 (4)^\circ$. The chelating phosphinite–phosphinous acid ligands display short, strong O–H–O hydrogen bonds (O(2)⋯O(3) = 2.424 (10), O(4)⋯O(5) = 2.429 (10) Å). The hydrogens of these systems are poorly located by X-ray diffraction but appear to lie close to the line joining the oxygen atoms (O(2)–H(69)–O(3) = $166 (7)^\circ$, O(4)–H(68)–O(5) = $167 (7)^\circ$). The P–O bond lengths are shorter than would be expected for Ph_2POR “single” bonds (e.g. in $\text{Mo}(\text{CO})(\text{PPh}_2\text{OH})(\text{PPh}_2\text{OCH}_2\text{CH}_2\text{NMe}_2)$ ⁴⁰ P–O(C) = 1.638 Å) and show little variation (1.546 (6)–1.560 (6) Å). The PtP_2O_4 ring systems are puckered, having intra-ring dihedral angles as follows: Pt(1)–P(2)–O(2)⋯O(3) = 7.8° , P(2)–O(2)⋯O(3)–P(3) = 20.9° , O(2)⋯O(3)–P(3)–Pt(1) = -39.6° , O(3)–P(3)–Pt(1)–P(2) = 41.8° , P(3)–Pt(1)–P(2)–O(2) = -24.7° , Pt(2)–P(4)–O(4)⋯O(5) = -4.0° , P(4)–O(4)⋯O(5)–P(5) = 26.1° , O(4)⋯O(5)–P(5)–Pt(2) = -34.7° , O(5)–P(5)–Pt(2)–P(4) = 31.3° , P(5)–Pt(2)–P(4)–O(4) = -11.3° . Related and different conformations may be observed in other mononuclear and dinuclear complexes involving this ligand (e.g. $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{O-H-OPPh}_2)]\text{Et}_4\text{N}$,⁴¹ $[\text{Mn}(\text{CO})_4(\text{PPh}_2\text{O-H-OPPh}_2)]$,⁴¹ $[\text{Rh}_2\text{Cl}_5(\text{PPh}_2\text{O-H-OPPh}_2)_2]\text{AsPh}_4$ ⁴²). Clearly this pseudo-five-membered ring is flexible.

Experimental Section

General Comments. All reactions were carried out under an Ar or N_2 atmosphere. Solvents were distilled from Na (toluene or hexane) or Na/benzophenone (ether, THF) prior to use. All commercially available chemicals were used as received. Complex 1 was prepared in nearly quantitative yield by the method reported⁶ or by the method used for compounds 2–7. ^1H and ^{31}P NMR spectra were recorded on a Bruker WH-250 or Varian XL-200 instrument. ^{31}P chemical shifts are reported with external H_3PO_4 as the standard. ^1H NMR spectral data are referenced versus the proton impurities in the deuterated solvents (benzene,

(37) Monojlević-Muir, Lj.; Muir, K. W.; Solomun, T. *Acta Crystallogr.* 1979, B35, 1237.

(38) Balch, A. L. In *Homogeneous Catalysis with Metal Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 167.

(39) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlević-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *J. Organomet. Chem.* 1980, 198, C33.

(40) Cotton, F. A.; Falvello, L. R.; Tomas, M.; Gray, G. M.; Kraihanzel, C. S. *Inorg. Chim. Acta* 1984, 82, 129.

(41) Fairzi, R.; Hiller, W.; Lorenz, I.-P.; Mohyla, J.; Zeiher, C. *J. Organomet. Chem.* 1984, 262, C43.

(42) Duncan, J. A. S.; Stephenson, T. A.; Walkinshaw, M. D.; Hedden, W. D.; Roundhill, D. M. *J. Chem. Soc., Dalton Trans.* 1984, 801.

δ 7.15; chloroform, δ 7.21; dichloromethane, δ 5.32). Pressure experiments were carried out in Teflon-lined, magnetically stirred autoclaves (100 mL). Microanalyses were performed by Analytische Laboratorien, Elbach, West Germany.

Preparation of Tris(diphenylphosphinous acid)platinum (2). To a stirred solution of Pt(PPh₃)₄ (5.5 g, 5.0 mmol) in benzene (100 mL) was added Ph₂POH (25.0 mmol), upon which the color changed from orange to yellow. After the mixture was stirred for 0.5 h at room temperature, dry ethyl ether (100 mL) was added and a white precipitate gradually formed. The precipitate was filtered off, washed with ether and dichloromethane, and dried under vacuum to yield 3.1 g (75%) of **2**. This compound is insoluble in most organic solvents. Anal. Calcd for C₃₆H₃₃O₃P₃Pt: C, 53.94; H, 4.15; P, 11.59; Pt, 24.34. Found: C, 54.07; H, 4.25; P, 11.75; Pt, 24.20.

(Ph₂POH)(Ph₂PO)HPt(Ph₂PCH₂CH=CH₂) (3). To a heterogeneous mixture of **2** (2.0 g, 2.5 mmol) and dichloromethane (20 mL) was added diphenylallylphosphine (2.5 mmol). The reaction mixture was stirred for 0.5 h at room temperature. During this time the solution became almost colorless. The solution was filtered, and to the filtrate was added 40 mL of methanol. The volume of this solution was concentrated under reduced pressure to approximately 25 mL. The white crystals formed in this solution were filtered off, washed with methanol, and dried under vacuum. The yield was 1.8 g (90%). ¹H NMR (CDCl₃): δ 6.8–8.0 (m, 30 H), 4.90 (m, 2 H), 5.50 (m, 1 H), 2.95 (m, 2 H), -4.30 (hydride, J_{Pt-H} = 868 Hz, $J_{P-H}(trans)$ = 163 Hz, $J_{P-H}(cis)$ = 9 and 24 Hz, 1 H). Anal. Calcd for C₃₉H₃₇O₂P₃Pt: C, 56.77; H, 4.52. Found: C, 56.85; H, 4.48.

(Ph₂POH)(Ph₂PO)HPt(Ph₂PCH=CH₂) (4). Complex **4** was prepared by using the same procedure as for **3**; yield 82%. ¹H NMR (toluene-*d*₆): δ 6.4–8.0 (m, 30 H), 5.70 (m, 1 H), 5.00 (m, 2 H), -3.95 (hydride, J_{Pt-H} = 868 Hz, $J_{P-H}(trans)$ = 163 Hz, $J_{P-H}(cis)$ = 9 and 23 Hz, 1 H). Anal. Calcd for C₃₈H₃₅O₂P₃Pt: C, 56.27; H, 4.35. Found: C, 56.18; H, 4.39.

(Ph₂POH)(Ph₂PO)HPt[P(CH₂CH=CH₂)₃] (5) and 11. To a suspension of **2** (1.0 mmol) in CDCl₃ (1 mL) was added triallylphosphine (1.0 mmol). All the solid dissolved, and a clear solution was formed. Product **5** was isolated by column chromatography over silica with dichloromethane/ethyl acetate (10/1 v/v) as the eluent. The yield after evaporation of the solvents was 0.6 g (80%). ¹H NMR of **5** (CDCl₃): δ 6.8–7.8 (m, 20 H), 5.50 (m, 3 H), 4.85 (m, 6 H), 2.20 (m, 6 H), -4.15 (hydride, J_{Pt-H} = 884 Hz, $J_{P-H}(trans)$ = 164 Hz, $J_{P-H}(cis)$ = 11 and 26 Hz, 1 H). A 0.3-g amount of **5** was heated in benzene (3 mL) at 80 °C for 3 h. According to ³¹P NMR the formation of **11** was almost quantitative. After evaporation of the benzene the residue was washed with methanol and dried in vacuo. The yield was 0.25 g (83%). ¹H NMR (CDCl₃): δ 7.0–7.9 (m, 20 H), 5.50 (m, 2 H), 4.90 (m, 4 H), 1.2–2.4 (m, 10 H). Anal. Calcd for C₃₃H₃₇O₂P₃Pt: C, 52.63; H, 4.95. Found for **5**: C, 52.70; H, 4.90. Found for **11**: C, 52.77; H, 4.92.

(Ph₂POH)(Ph₂PO)HPt(Ph₂POC₂H₄CH=CH₂) (6) and 12. Ph₂POC₂H₄CH=CH₂ was prepared by reacting Ph₂POCl with 1 equiv of the alcohol in dry CH₂Cl₂ containing 10% (v/v) of pyridine. The butenyl phosphinite was not isolated, but the solution was used as such after removal of the py·HCl salt by filtration (³¹P NMR δ +110.3 ppm). Isolation of **6** was identical with that for **5**. The yield after evaporation of the solvents was 1.20 g (70%). ¹H NMR (CDCl₃): δ 6.9–7.9 (m, 30 H), 5.33 (m, 1 H), 4.43 (m, 2 H), 3.38 (m, 2 H), 2.03 (m, 2 H), -4.12 (hydride, J_{Pt-H} = 888 Hz, $J_{P-H}(trans)$ = 157 Hz, $J_{P-H}(cis)$ = 11 and 25 Hz, 1 H). A 0.6-g amount of **6** was refluxed for 0.5 h in benzene to give **12**. After evaporation of the solvent **12** was obtained in quantitative yield. ¹H NMR (CDCl₃): δ 6.8–8.0 (m, 30 H), 3.8–4.2 (m, 2 H), 1.5–2.2 (m, 3 H), 0.35 (m, 3 H). Anal. Calcd for C₄₀H₃₉O₃P₃Pt: C, 56.18; H, 4.60. Found for **6**: C, 56.01; H, 4.60. Found for **12**: C, 56.07; H, 4.56.

(Ph₂POH)(Ph₂PO)HPt(Ph₂POC₂H₄C≡CH) (7). The phosphinite ligand was prepared and used as described for **6** (³¹P NMR +112.3 ppm). The procedure followed was similar to that for **3**; the yield was 65%. ¹H NMR of **7** (C₆D₆): δ 6.6–8.3 (m, 30 H), 3.30 (q, 7 Hz, J_{P-H} = J_{H-H} , 2 H), 1.75 (t, 7 Hz, d, 2.5 Hz, 2 H), 1.61 (t, 2.5 Hz, 1 H), -4.03 (hydride, J_{Pt-H} = 880 Hz, $J_{P-H}(trans)$ = 157 Hz, $J_{P-H}(cis)$ = 12 and 25 Hz, 1 H). Anal. Calcd for C₄₀H₃₇O₃P₃Pt: C, 56.31; H, 4.37. Found: C, 56.16; H, 4.37.

Table IV. Crystallographic Data for **10** and **17a**·C₇H₈

compd	10	17a ·C ₇ H ₈
formula	C ₃₆ H ₃₅ O ₂ P ₃ Pt	C ₆₀ H ₅₃ O ₄ P ₅ Pt ₂ ·C ₇ H ₈
fw	811.7	1475.2
space group	P2 ₁ /c	P2 ₁ /n
a, Å	10.622 (2)	15.745 (3)
b, Å	13.217 (3)	15.151 (2)
c, Å	24.563 (5)	25.677 (5)
β , deg	96.66 (2)	99.45 (2)
V, Å ³	3425 (1)	6043 (2)
Z	4	4
d_{calc} , g/cm ³	1.574	1.622
cryst size, mm	0.08 × 0.22 × 0.42	0.2 × 0.35 × 0.4
μ (Mo K α), cm ⁻¹	43.1	48.54
no. of orientn rflns	15	15
range, deg	28 < 2 θ < 30	28 < 2 θ < 30
scan method	ω (Wyckoff)	ω (Wyckoff)
data collectn range, deg	4 < 2 θ < 50	4 < 2 θ < 50
decay, %	0	0
no. of unique data	4602	8368
no. of total data used	4218 ($I > 2\sigma(I)$)	7331 ($I > 2\sigma(I)$)
no. of refined params	400	712
transmissn factors	0.710–0.367	0.047–0.019
R^a	0.031	0.037
R_w^b	0.032	0.037
$g(\text{weights})^c$	0.0004	0.0006
quality of fit ^d	0.99	1.04
resid peaks, e/Å ³	0.52 (<1 Å from Pt)	0.72 (<1 Å from Pt)

$$^a R = \sum |\Delta| / \sum |F_o|, \Delta = |F_o| - |F_c|. \quad ^b R_w = \sum w^{1/2} |\Delta| / \sum w^{1/2} |F_o|. \quad ^c w = [\sigma_c^2(F_o) + gF_o^2]^{-1}. \quad ^d S = [\sum w \Delta^2 / (N_{obs} - N_{par})]^{1/2}.$$

(Diphenylphosphinito)(diphenylphosphinous acid)-1,1-diphenyl-1-phospha-2-platinacyclopentane (8). A solution of compound **3** (0.5 g) in toluene (20 mL) was heated at 90 °C for 1 h. The toluene was evaporated, and the residue was washed with methanol to give cream-colored crystals of **8**, yield 0.459 g (88%). ¹H NMR: δ 6.80–8.00 (m, 30 H), 2.10 (m, 2 H), 1.60–1.80 (m, 4 H). Anal. Calcd for C₃₉H₃₇O₂P₃Pt: C, 56.77; H, 4.52. Found: C, 57.02; H, 4.53.

(Diphenylphosphinito)(diphenylphosphinous acid)-1,1-diphenyl-1-phospha-2-platinacyclopropane (9) and (Diphenylphosphinito)(diphenylphosphinous acid)-1,1-diphenyl-1-phospha-2-platinacyclobutane (10). A solution of **4** (1.1 g, 1.36 mmol) in 20 mL of benzene was refluxed for 0.25 h. According to ¹H NMR spectroscopy a mixture was formed of **9** and **10** in a ratio of 3:1. The benzene was replaced by methanol (10 mL). The crystals formed on standing were also a mixture. A second crop of crystals formed on standing consisted of >95% pure **9**. Pure **10** was prepared by refluxing the mixture in toluene for 2 h. This solution was concentrated, and when it was cooled, crystals of **10** separated. Recrystallization from toluene gave pure **10**. Combined yields of **9** and **10** are over 90%. ¹H NMR (CDCl₃): **9**, δ 7.0–7.8 (m, 30 H), 1.63 (m, 1 H), 0.90 (m, 3 H); **10**, δ 7.0–7.8 (m, 30 H), 3.95 (m, 2 H), 1.00 (m, 2 H). Anal. Calcd for C₃₈H₃₅O₂P₃Pt: C, 56.23; H, 4.35; P, 11.45; Pt, 24.03. Found for **9**: C, 56.32; H, 4.45; P, 11.54; Pt, 23.85. Found for **10**: C, 56.40; H, 4.48; P, 11.38; Pt, 24.10.

Complexes 13a and 13b. A 0.043-g (0.05-mmol) amount of **7** was dissolved in 0.6 mL of C₆D₆ and refluxed under argon for 1.5 h. Conversion to **13a** was >90% according to ³¹P NMR. ¹H NMR (C₆D₆): **13a**, δ 7.0–7.8 (m, 30 H), 5.8 (J_{Pt-H} = 90 Hz, J_{P-H} = 16 Hz, 1 H), 4.8 (J_{Pt-H} = 45 Hz, J_{P-H} = 7 Hz, 1 H) (olefinic hydrogens), 4.06 (m, 2 H, O-CH₂), 2.25 (dd, 2 H). For **13b**, the crude reaction mixture of **7** (2.0 mmol) still containing diphenylphosphinous acid was refluxed in benzene for 0.5 h. The benzene was removed under vacuum. The solid was dissolved in dichloromethane and the solution chromatographed over silica with dichloromethane/ethyl acetate (1/1 v/v) as the eluent. The yield of **13b** after removal of the solvents was 1.0 g (59%). ¹H NMR (C₆D₆): δ 6.5–8.0 (m, 30 H), 5.00 (m, 1 H), 2.05 (m, 2 H), 1.75 (m, 3 H).

Complex 14. The phosphinite ligand was prepared as described for **6** (³¹P NMR (Ph₂POC₂H₄CH=CH₂) δ +112.3 ppm). The reaction mixture of **2** (2.0 mmol) and the ligand (2.0 mmol) was refluxed in CH₂Cl₂ for 5 min. The procedure for the isolation

Table V. Selected Bond Lengths and Bond Angles for 10

Bond Lengths (Å)			
Pt-P(1)	2.319 (2)	Pt-P(2)	2.305 (2)
Pt-P(3)	2.288 (2)	Pt-C(1)	2.121 (6)
P(1)-C(2)	1.819 (7)	P(1)-C(3)	1.816 (6)
P(1)-C(9)	1.814 (7)	P(2)-O(2)	1.580 (5)
P(2)-C(15)	1.816 (6)	P(2)-C(21)	1.818 (6)
P(3)-O(3)	1.537 (4)	P(3)-C(27)	1.826 (6)
P(3)-C(33)	1.820 (7)	O(2)-H	0.786 (74)
C(1)-C(2)	1.573 (9)		
Bond Angles (deg)			
P(1)-Pt-P(2)	106.2 (1)	P(1)-Pt-P(3)	162.6 (1)
P(2)-Pt-P(3)	91.1 (1)	P(1)-Pt-C(1)	68.3 (2)
P(2)-Pt-C(1)	174.5 (2)	P(3)-Pt-C(1)	94.4 (2)
Pt-P(1)-C(2)	88.1 (2)	Pt-P(1)-C(3)	117.6 (2)
C(2)-P(1)-C(3)	107.7 (3)	Pt-P(1)-C(9)	123.4 (2)
C(2)-P(1)-C(9)	110.3 (3)	C(3)-P(1)-C(9)	107.1 (3)
Pt-P(2)-O(2)	114.4 (2)	Pt-P(2)-C(15)	115.2 (2)
O(2)-P(2)-C(15)	102.5 (2)	Pt-P(2)-C(21)	115.2 (2)
O(2)-P(2)-C(21)	106.1 (3)	C(15)-P(2)-C(21)	101.8 (3)
Pt-P(3)-O(3)	116.7 (2)	Pt-P(3)-C(27)	108.4 (2)
O(3)-P(3)-C(27)	106.7 (2)	Pt-P(3)-C(33)	113.6 (2)
O(3)-P(3)-C(33)	106.3 (3)	C(27)-P(3)-C(33)	104.3 (3)
P(2)-O(2)-H	100.3 (49)	Pt-C(1)-C(2)	102.4 (4)
P(1)-C(2)-C(1)	94.6 (4)		

Table VI. Positional Parameters ($\times 10^4$) and Their Standard Deviations for 10

	x	y	z
Pt	3245 (1)	7357 (1)	7474 (1)
P(1)	3867 (2)	6377 (1)	8242 (1)
P(2)	2018 (2)	8643 (1)	7764 (1)
P(3)	2920 (2)	7932 (1)	6591 (1)
O(2)	2051 (4)	9656 (3)	7424 (2)
O(3)	2368 (4)	9003 (3)	6505 (2)
C(1)	4416 (6)	6134 (4)	7288 (3)
C(2)	4319 (7)	5395 (4)	7784 (3)
C(3)	5285 (6)	6760 (5)	8678 (3)
C(4)	6248 (7)	6083 (6)	8842 (3)
C(5)	7335 (7)	6425 (6)	9153 (3)
C(6)	7485 (7)	7411 (6)	9293 (3)
C(7)	6530 (7)	8099 (6)	9144 (3)
C(8)	5450 (6)	7773 (5)	8827 (3)
C(9)	2767 (6)	5876 (5)	8686 (3)
C(10)	2991 (8)	5860 (5)	9246 (3)
C(11)	2084 (9)	5496 (6)	9561 (3)
C(12)	966 (9)	5160 (7)	9316 (4)
C(13)	693 (8)	5155 (6)	8756 (4)
C(14)	1598 (7)	5523 (5)	8443 (3)
C(15)	2467 (5)	9071 (4)	8462 (3)
C(16)	2160 (6)	8507 (5)	8906 (3)
C(17)	2605 (7)	8771 (6)	9438 (3)
C(18)	3351 (8)	9627 (7)	9530 (3)
C(19)	3640 (7)	10204 (6)	9100 (4)
C(20)	3220 (6)	9941 (5)	8569 (3)
C(21)	353 (5)	8337 (4)	7775 (2)
C(22)	-457 (6)	9016 (5)	7981 (3)
C(23)	-1718 (7)	8771 (7)	7994 (3)
C(24)	-2180 (7)	7859 (7)	7814 (3)
C(25)	-1393 (7)	7186 (6)	7597 (3)
C(26)	-113 (6)	7420 (5)	7584 (3)
C(27)	1817 (6)	7076 (4)	6195 (2)
C(28)	548 (7)	7310 (6)	6125 (4)
C(29)	-347 (8)	6626 (8)	5888 (4)
C(30)	30 (8)	5736 (6)	5687 (3)
C(31)	1261 (8)	5489 (6)	5753 (3)
C(32)	2160 (6)	6154 (5)	6006 (3)
C(33)	4337 (6)	7899 (4)	6239 (2)
C(34)	5520 (6)	8000 (5)	6532 (3)
C(35)	6606 (7)	8096 (5)	6263 (3)
C(36)	6490 (7)	8094 (6)	5707 (3)
C(37)	5313 (8)	7967 (6)	5405 (3)
C(38)	4244 (7)	7892 (5)	5665 (3)
H	2256 (65)	9444 (52)	7148 (29)

of 14 was the same as that for 5. The yield was 1.7 g (80%). ^1H NMR (CDCl_3): δ 6.6-7.9 (m, 30 H), 3.90 (m, 2 H), 2.18 (m, 1 H),

Table VII. Selected Bond Lengths and Bond Angles for 17a•C₇H₈

Bond Lengths (Å)			
Pt(1)-Pt(2)	2.907 (1)	Pt(1)-P(1)	2.295 (2)
Pt(1)-P(2)	2.318 (2)	Pt(1)-P(3)	2.275 (2)
Pt(1)-H	1.645 (60)	Pt(2)-P(1)	2.308 (2)
Pt(2)-P(4)	2.333 (2)	Pt(2)-P(5)	2.279 (2)
Pt(2)-H	1.937 (68)	P(1)-C(1)	1.813 (7)
P(1)-C(7)	1.800 (8)	P(2)-O(2)	1.560 (6)
P(2)-C(13)	1.814 (8)	P(2)-C(19)	1.812 (8)
P(3)-O(3)	1.556 (6)	P(3)-C(25)	1.815 (8)
P(3)-C(31)	1.837 (9)	P(4)-O(4)	1.557 (6)
P(4)-C(37)	1.822 (8)	P(4)-C(43)	1.825 (8)
P(5)-O(5)	1.546 (5)	P(5)-C(49)	1.815 (8)
P(5)-C(55)	1.798 (9)	O(2)-H(69)	0.760 (83)
O(4)-H(68)	0.831 (93)		
Bond Angles (deg)			
Pt(2)-Pt(1)-P(1)	51.0 (1)	Pt(2)-Pt(1)-P(2)	119.8 (1)
P(1)-Pt(1)-P(2)	170.7 (1)	Pt(2)-Pt(1)-P(3)	151.0 (1)
P(1)-Pt(1)-P(3)	100.7 (1)	P(2)-Pt(1)-P(3)	88.6 (1)
Pt(2)-Pt(1)-H	39.3 (23)	P(1)-Pt(1)-H	88.2 (23)
P(3)-Pt(1)-H	82.6 (23)	P(3)-Pt(1)-H	168.8 (24)
Pt(1)-Pt(2)-P(1)	50.7 (1)	Pt(1)-Pt(2)-P(4)	117.6 (1)
P(1)-Pt(2)-P(4)	164.8 (1)	Pt(1)-Pt(2)-P(5)	151.0 (1)
P(1)-Pt(2)-P(5)	101.4 (1)	P(4)-Pt(2)-P(5)	91.2 (1)
Pt(1)-Pt(2)-H	32.5 (18)	P(1)-Pt(2)-H	81.3 (18)
P(4)-Pt(2)-H	85.6 (18)	P(5)-Pt(2)-H	175.8 (18)
Pt(1)-P(1)-Pt(2)	78.3 (1)	Pt(1)-P(1)-C(1)	111.4 (3)
Pt(2)-P(1)-C(1)	109.0 (2)	Pt(1)-P(1)-C(7)	119.8 (3)
Pt(2)-P(1)-C(7)	123.8 (2)	Pt(1)-P(2)-O(2)	114.5 (2)
Pt(1)-P(2)-C(13)	117.8 (3)	Pt(1)-P(2)-C(19)	106.6 (3)
Pt(1)-P(3)-O(3)	112.5 (2)	Pt(1)-P(3)-C(25)	108.1 (3)
Pt(1)-P(3)-C(31)	119.2 (3)	Pt(2)-P(4)-O(4)	115.3 (2)
Pt(2)-P(4)-O(4)	115.3 (2)	Pt(2)-P(4)-C(37)	116.8 (3)
Pt(2)-P(4)-C(43)	109.5 (2)	Pt(2)-P(5)-O(5)	112.5 (2)
Pt(2)-P(5)-C(49)	112.5 (2)	Pt(2)-P(5)-C(49)	113.1 (3)
Pt(2)-P(5)-C(55)	117.1 (3)	P(2)-O(2)-H(69)	107.7 (65)
P(4)-O(4)-H(68)	113.9 (54)		

0.40 (m, 3 H). Anal. Calcd for C₃₉H₃₇O₃P₃Pt: C, 55.69; H, 4.43. Found: C, 55.76; H, 4.48.

Complex 15. A 0.086-g (0.10-mmol) amount of compound 1 and 0.026 g (0.10 mmol) of Ph₂PC₂H₄COOH were dissolved in 2 mL of toluene, and this solution was refluxed for 2 h. ^{31}P NMR showed the formation of 15 in 70% yield.

Carbon Monoxide Insertions. 16. Solutions of 10-14 (0.2 mmol) in toluene (15 mL) were stirred in an autoclave under 40 bar of carbon monoxide pressure for 1.0 h at 85 °C. After the gases had been vented, the toluene was evaporated and the residue dissolved in CDCl₃ (0.7 mL) to run a ^{31}P NMR spectrum. In this manner 12 was converted into 16 (65%).

Platinum Dimers 17a-d. Decomposition of 1 under Hydroformylation Conditions. A solution of 1 (0.86 g, 1.0 mmol) in benzene (20 mL) was stirred in an autoclave under an atmosphere of carbon monoxide and ethene (1:1, 20 bar) for 24 h at 85 °C. Aliquots (1 mL) were taken after 0.5, 2.5, 4.0, and 8.0 h. From these samples the benzene was distilled off and the remaining residue was dissolved in CDCl₃ (0.7 mL). These solutions were analyzed by ^1H and ^{31}P NMR spectroscopy. Proton NMR indicated the presence of the mixed anhydride of propionic acid and diphenylphosphinous acid and the platinum acyl complex 18. The proton NMR of 18 containing the mixed anhydride as the ligand L is clearly different from the proton NMR of 19, the ethyl phosphinite complex (vide infra). ^1H NMR of 18: δ 2.35 (m, 2 H), 1.1 (t, 3 H) (propionic phosphinic anhydride), 0.03 (t, 3 H), 1.36 (q, 2 H) (Pt-propionyl).

After 24 h the resulting red solution in toluene was reduced in volume to approximately 5 mL. After this solution stood at room temperature for 80 h yellow crystals of 17a separated off (0.45 g, 65%). The procedure was repeated with tri-*p*-tolylphosphine instead of triphenylphosphine in 1 for 2.5 h at 100 °C. The yield of 17a was 0.4 g, and according to ^1H NMR no tolyl groups were present.

Preparation of 17a. To a heterogeneous mixture of 2 (2.4 g, 3.0 mmol) and CH₂Cl₂ (20 mL) was added diphenylphosphine (0.56 g, 3.0 mmol). The reaction mixture was stirred for 30 min. The solution was filtered, and 25 mL of methanol was added and

Table VIII. Positional Parameters ($\times 10^4$) and Their Standard Deviations for 17a \cdot C₇H₈

	x	y	z		x	y	z
Pt(1)	5642 (1)	6467 (1)	7358 (1)	C(31)	6849 (5)	5757 (6)	8578 (3)
Pt(2)	4113 (1)	7573 (1)	7229 (1)	C(32)	7211 (6)	6547 (8)	8756 (4)
P(1)	4943 (1)	7058 (1)	7994 (1)	C(33)	7426 (8)	6700 (11)	9304 (6)
P(2)	6201 (1)	6014 (1)	6621 (1)	C(34)	7227 (10)	6045 (14)	9644 (5)
P(3)	6623 (1)	5587 (1)	7860 (1)	C(35)	6906 (10)	5293 (11)	9469 (5)
P(4)	3630 (1)	8162 (1)	6394 (1)	C(36)	6685 (7)	5117 (7)	8929 (3)
P(5)	2974 (1)	8171 (1)	7549 (1)	C(37)	3577 (5)	7411 (5)	5835 (3)
O(2)	7154 (4)	5692 (4)	6740 (2)	C(38)	2849 (6)	6881 (6)	5722 (3)
O(3)	7529 (3)	5638 (4)	7693 (2)	C(39)	2752 (8)	6278 (7)	5304 (4)
O(4)	2702 (3)	8549 (4)	6311 (2)	C(40)	3376 (8)	6219 (7)	4999 (4)
O(5)	2159 (3)	8235 (4)	7124 (2)	C(41)	4089 (7)	6735 (7)	5099 (4)
C(1)	5542 (5)	7972 (5)	8331 (3)	C(42)	4196 (6)	7331 (6)	5513 (3)
C(2)	6129 (5)	8382 (5)	8057 (3)	C(43)	4347 (5)	9052 (5)	6262 (3)
C(3)	6561 (6)	9147 (6)	8257 (4)	C(44)	4225 (6)	9493 (6)	5784 (4)
C(4)	6392 (7)	9505 (7)	8713 (4)	C(45)	4738 (7)	10198 (7)	5703 (4)
C(5)	5387 (6)	8353 (6)	8789 (3)	C(46)	5400 (7)	10472 (7)	6090 (5)
C(6)	5812 (7)	9116 (7)	8988 (4)	C(47)	5529 (7)	10043 (7)	6569 (4)
C(7)	4544 (5)	6342 (5)	8458 (3)	C(48)	5006 (6)	9326 (6)	6653 (4)
C(8)	3854 (5)	5800 (5)	8274 (3)	C(49)	3197 (5)	9264 (5)	7828 (3)
C(9)	3540 (7)	5205 (6)	8596 (5)	C(50)	4011 (6)	9626 (5)	7922 (3)
C(10)	3891 (8)	5156 (7)	9129 (5)	C(51)	4121 (7)	10452 (6)	8160 (4)
C(11)	4573 (7)	5702 (7)	9329 (4)	C(52)	3439 (8)	10927 (6)	8278 (4)
C(12)	4912 (6)	6288 (6)	8992 (3)	C(53)	2643 (7)	10582 (6)	8182 (4)
C(13)	6232 (5)	6814 (5)	6098 (3)	C(54)	2501 (6)	9752 (6)	7956 (4)
C(14)	6254 (6)	6551 (7)	5582 (3)	C(55)	2605 (5)	7600 (5)	8083 (3)
C(15)	6413 (7)	7195 (9)	5217 (4)	C(56)	2971 (6)	7273 (6)	8614 (3)
C(16)	6558 (8)	8055 (8)	5372 (4)	C(57)	2684 (7)	7246 (6)	9005 (4)
C(17)	6535 (6)	8301 (7)	5873 (4)	C(58)	2040 (8)	6642 (7)	8894 (5)
C(18)	6364 (5)	7694 (6)	6245 (3)	C(59)	1658 (7)	6527 (7)	8388 (5)
C(19)	5560 (5)	5079 (5)	6348 (3)	C(60)	1928 (6)	6994 (6)	7972 (4)
C(20)	4677 (6)	5145 (7)	6220 (4)	C(61)	4156 (14)	8439 (9)	270 (7)
C(21)	4170 (8)	4427 (8)	6102 (5)	C(62)	3807 (13)	8051 (12)	676 (8)
C(22)	4542 (10)	3596 (9)	6127 (4)	C(63)	4214 (14)	7440 (11)	949 (8)
C(23)	5421 (9)	3508 (6)	6250 (4)	C(64)	4999 (13)	7140 (14)	876 (8)
C(24)	5933 (7)	4255 (6)	6354 (3)	C(65)	5384 (14)	7453 (16)	557 (9)
C(25)	6255 (5)	4453 (5)	7772 (3)	C(66)	4997 (21)	8162 (18)	209 (9)
C(26)	5392 (6)	4240 (6)	7711 (4)	C(67)	3754 (19)	9076 (14)	-42 (9)
C(27)	5099 (8)	3372 (7)	7628 (5)	H	5087 (41)	7144 (41)	6930 (25)
C(28)	5717 (11)	2729 (8)	7598 (5)	H(68)	2439 (55)	8455 (53)	6560 (33)
C(29)	6564 (10)	2920 (7)	7665 (5)	H(69)	7261 (53)	5595 (54)	7034 (33)
C(30)	6832 (7)	3779 (6)	7766 (4)				

part of the dichloromethane distilled off. The orange solution was left overnight. The solution turned deep red. The methanol was distilled off under reduced pressure, and the red residue was dissolved in toluene (15 mL). Yellow crystals of 17a separated from the red solution, which were filtered off and recrystallized from toluene (1.2 g, 58%). Anal. Calcd for C₆₀H₅₃O₄P₅Pt₂C₇H₈: C, 54.55; H, 4.17; P, 10.50; Pt, 26.45. Found: C, 55.37; H, 4.31; P, 10.06; Pt, 25.75.

In situ Preparation of 17d. To a solution of 1 (0.85 g) in toluene was added 0.5 mL of acetic anhydride. The reaction mixture was refluxed for 15 min, upon which the color changed to deep red. According to ³¹P NMR of this solution over 80% of compound 17d was formed (albeit with the acetic anhydride rather than the propionic anhydride, which is obtained during hydroformylation with ethene). Attempts to isolate this compound failed (chromatography over silica with dichloromethane, ether, or methanol). The product isolated eventually was 17a.

Preparation of 19. When 2 was reacted in a slurry with a stoichiometric amount of ethyl diphenylphosphinite, the hydride precursor to 19 was obtained, (Ph₂PO-H-OPPh₂)PtH-(Ph₂POCH₂CH₃). Reaction in benzene under pressure of CO and ethene (35 bar, 1:1) for 1 h at 80 °C gave 19 in >90% yield according to ³¹P NMR. Isolated yield following the procedure for 5 was 65%. ¹H NMR (CDCl₃): δ 6.6–8.0 (m, 30 H), 3.22 (m, 2 H), 1.25 (m, 2 H), 0.61 (t, 3 H), -0.07 (t, 3 H). Anal. Calcd for C₄₀H₄₁O₄P₃Pt: C, 55.02; H, 4.73. Found: C, 54.99; H, 4.58.

Crystal Structure Determinations. Compound 10 was crystallized from toluene. A single crystal was mounted with epoxy glue on a thin glass fiber in air. All diffraction experiments were conducted at room temperature on a Nicolet P3m diffractometer using graphite-monochromated Mo K α X-radiation ($\lambda = 0.71069$ Å). Three check reflections measured repeatedly during data collection showed no significant variation in intensity. An ab-

sorption correction was applied, based on the indexed crystal faces.

The structure was solved by conventional heavy-atom (Patterson and difference Fourier) methods. All non-hydrogen atoms were assigned anisotropic thermal parameters. All phenyl and methyl hydrogens were assigned idealized geometries (H-C = 0.96 Å) with isotropic vibration parameters $U_{\text{iso}} = \text{ca. } 1.2$ times that of their carbon atom. The hydrogen atoms H(1a), H(1b), H(2a), H(2b), and H were located in difference electron density syntheses. H was refined without positional constraints, with a fixed isotropic U . The structure was refined by full-matrix blocked-cascade least squares. All calculations were carried out on a Data General Eclipse (R) computer using programs of the SHELXTL-PLUS package.⁴³ Complex neutral-atom scattering factors were taken from the literature⁴⁴ for all atoms. Table V lists selected bond lengths and angles. Details of the data collection and structure determination are gathered in Table IV; positional and equivalent isotropic thermal parameters are given in Table VI.

The structure of 17a as its toluene solvate was determined on a crystal cleaved from a larger block. The structure determination was carried out as described above, with the following differences. The intensity data were corrected for absorption effects by calculation of transmission coefficients based on a six-parameter fit to 200 azimuthal scan data. Hydrogen atoms H and H(68) were located in difference electron density synthesis, while H(69) was placed at the midpoint of O(2)–O(3). These three hydrogen atoms were refined without positional constraints, with fixed isotropic U 's. Further details of the structure analysis are given in Table

(43) Sheldrick, G. M. SHELXTL (Rev. 4.1), Programs for use in the Nicolet R3m.E system; University of Göttingen, Göttingen, FRG, 1984.

(44) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV.

