Articles

Asymmetric Hydroformylation of Styrene Catalyzed by Platinum(II)−Alkyl Complexes Containing Atropisomeric Diphosphines

Alberto Scrivanti,* Valentina Beghetto, Alessandra Bastianini, and Ugo Matteoli*

Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30123 Venezia, Italy

Gloria Menchi

Dipartimento di Chimica Organica, Università di Firenze, Via G. Capponi 9, 50121 Firenze, Italy

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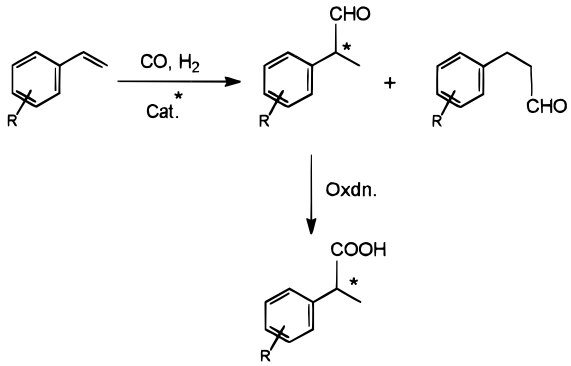
The complexes [Pt(CH_3)Cl(P−P)] **1**−**3** (**1**, P−P = (*S*)-6,6′-(dimethoxybiphenyl)-2,2′-diylbis-(diphenylphosphine) ((*S*)-MOBIPH); **2**, P−P = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP); **3**, P−P = (2*S*,3*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-(diphenylphosphino)-butane ((*S*,*S*)-DIOP)) in the presence of $SnCl_2$ catalyze the asymmetric hydroformylation of styrene. The reaction proceeds under mild conditions (50 °C, $P(H_2) = P(CO) = 50$ atm) to give the desired branched aldehyde with moderate regioselectivity. Good enantioselectivities (up to 75%) have been obtained using [Pt(CH_3)Cl{(*S*)-MOBIPH}]. The influence of solvent, temperature, $P(H_2)$, and $P(CO)$ has been studied. An impressive influence of the solvent has been observed: using [Pt(CH_3)Cl{(*R*)-BINAP}], the chirality of 2-phenylpropanal obtained in toluene or in tetrahydrofuran is opposite to that of 2-phenylpropanal produced in dichloromethane or acetone. Using [Pt(CH_3)Cl{(*S*)-MOBIPH}] or [Pt(CH_3)Cl{(*R*)-BINAP}], an unusual increase of the rate and enantioselectivity of the reaction with increasing $P(CO)$ is observed. In order to get information on the reaction mechanism, the carbonylation of [Pt(CH_3)($SnCl_3$){(*S*)-MOBIPH}] (**4**) has been studied. This reaction carried out at room temperature and atmospheric pressure affords an equilibrium mixture containing the cationic alkyl complex [Pt(CH_3)(CO){(*S*)-MOBIPH}]$^+$[$SnCl_3$]$^-$ (**6**) and the neutral acyl species [Pt($COCH_3$)($SnCl_3$){(*S*)-MOBIPH}] (**7**). The carbonylation of [Pt(CH_3)($SnCl_3$){(*R*)-BINAP}] (**5**) proceeds in the same fashion to give [Pt(CH_3)(CO){(*R*)-BINAP}]$^+$[$SnCl_3$]$^-$ (**8**) and [Pt($COCH_3$)($SnCl_3$){(*R*)-BINAP}] (**9**).

Introduction

The asymmetric hydroformylation of prochiral olefins provides a very convenient entry to chiral aldehydes, which are useful intermediates employed for the preparation of important biologically active compounds.[1,2] For example, the asymmetric hydroformylation of vinylarenes has been widely studied to produce optically pure 2-aryl-substituted propanals, which are readily oxidized to the corresponding 2-arylpropanoic acids (Scheme 1), constituting an important class of nonsteroidal analgesics.[3,4]

Scheme 1



Until the important results recently obtained by Takaya and co-workers using Rh(I) complexes,[5] the most widely used catalysts in asymmetric hydroformylations were systems based on platinum(II) complexes of the type [$PtCl_2$(P−P)] (P−P = chiral chelating diphosphine

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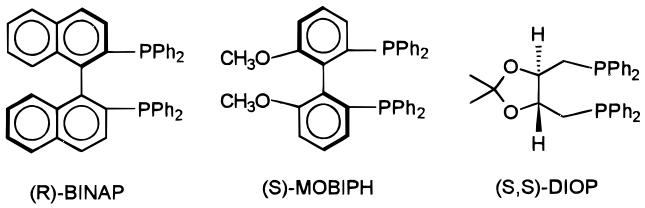
Table 1. Influence of Solvent on the Hydroformylation of Styrene Using the Catalytic System [Pt(CH$_3$)Cl{(*R*)-BINAP}]/SnCl$_2$[a]

			product composition (%)					
solvent	*t* (h)	conversn (%)	aldehydes	ethylbenzene	polymer	*b*/*n*	op[b] (%)	config
toluene	118	79.8	84.0	3.9	12.1	0.58	41.6	*R*
acetone	186	44.4	72.8	4.5	22.7	1.03	23.2	*S*
THF	498	17.2	52.3	7.0	40.7	0.56	20.0	*R*
CH_2Cl_2	42	13.2	84.1	7.6	8.3	1.08	15.0	*S*

[a] Styrene 50 mmol; [Pt(CH$_3$)Cl{(*R*)-BINAP}] 0.05 mmol; SnCl$_2$ 0.05 mmol; substrate/catalyst 1000/1; solvent 35 mL; $P(H_2) = P(CO)$ 50 atm; *T* 50 °C. [b] op, optical purity.



(R)-BINAP (S)-MOBIPH (S,S)-DIOP

Figure 1. Structures of the chiral ligands used.

ligand) promoted by SnCl$_2$.[6] With this type of catalyst, very high asymmetric inductions have been achieved using dibenzophospholyl-substituted diphosphines[7,8] or atropisomeric ligands such as BINAP[9,10] (Figure 1).

Unfortunately, the high enantioselectivities obtained with these Pt(II) catalysts are frequently accompanied by low regioselectivities to the desired branched aldehyde and poor reaction rates,[6] so there is a constant impulse to test and develop more active and selective catalytic systems.

In a previous study we observed that when the hydroformylation of styrene is carried out in the presence of the system [PtCl$_2${(*S*)-MOBIPH}]/SnCl$_2$ the enantioselectivity increases with increasing the carbon monoxide partial pressure.[10] Since such a trend contrasts with that usually found with similar systems,[6] we were prompted to further investigate the reaction and its mechanism.

Essential steps[6c,11,12] of the mechanism of the platinum-catalyzed hydroformylation are (i) insertion of the alkene into a Pt−H bond to give both linear and branched alkyl−Pt complexes, (ii) insertion of CO into the Pt−C bond to give the corresponding acyl species, and (iii) reaction of the acyl intermediates with molecular hydrogen and/or acid species to afford the aldehydes and restore the starting platinum hydride.

Since the asymmetric induction occurs, as suggested in the literature,[8,13] during the formation of the Pt−alkyl intermediates, no substantial influence on the optical purity should be played by the CO partial pressure. The favorable influence of this parameter on the enantioselectivity reported by us[10] is unprecedented and needs to be rationalized.

To get a better understanding of this effect we synthesized the alkyl platinum complexes of formulation [Pt(CH$_3$)Cl(P−P)] (**1**−**3**) (**1**, P−P = (*S*)-6,6′-dimethoxybiphenyl-2,2′-diylbis(diphenylphosphine) ((*S*)-MOBIPH); **2**, P−P = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP); **3**, P−P = (2*S*,3*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-(diphenylphosphino)butane ((*S*,*S*)-DIOP)). Their catalytic behavior in the presence of SnCl$_2$ has been fully investigated by studying the influence of some variables, such as $P(CO)$, $P(H_2)$, temperature, and nature of the solvent. Finally, the catalytic activity of complexes **1**−**3** has been compared with that of the analogue dichloro−Pt(II) complexes.

Since it is reasonable to hypothesize that the *P*(CO) plays a crucial role in the formation of the acyl species, we have also studied the insertion of CO into the Pt−CH$_3$ bond of complexes **1** and **2** in the presence of SnCl$_2$ to get information on the mechanism and clarify the influence of *P*(CO) on the enantioselectivity.

Catalytic Studies. The platinum catalytic precursors were synthesized by reacting complex [Pt(CH$_3$)Cl(1,5-COD)] (1,5-COD = 1,5-cyclooctadiene) with an equimolecular amount of the appropriate diphosphine.[14]

The characterization of the resulting complexes [Pt(CH$_3$)Cl{(*S*)-MOBIPH}] (**1**), [Pt(CH$_3$)Cl{(*R*)-BINAP}] (**2**), and [Pt(CH$_3$)Cl{(*S*,*S*)-DIOP}] (**3**)[15] was done by elemental analysis and spectroscopic techniques (IR, ^{1}H and ^{31}P NMR). The data, reported in the Experimental Section, are in keeping with the proposed formulation.

Owing to our interest in the synthesis of 2-arylpropanoic acids, we have studied the hydroformylation of styrene.

The catalytic experiments were carried out as described in the Experimental Section by combining *in situ* equimolecular amounts of the complex **1**, **2**, or **3** and SnCl$_2$. The composition of the raw mixtures at the end of reactions was determined by GC using an internal standard. This procedure allowed us to quantify both the expected aldehydes and ethylbenzene and the polystyrene not detected by GC. The formation of the polymer was confirmed by IR spectroscopy. The optical purity of the branched aldehyde was determined by polarimetry using the specific rotatory power values reported by Consiglio.[16]

Since the use of Pt(II)−alkyl complexes **1**−**3** as catalyst precursors was unprecedented, we have first studied the influence of the solvent. The relevant data we obtained using complex **2** are reported in Table 1. They indicate that the solvent plays a peculiar role in influencing all the aspects of the catalytic activity. The

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Table 2. Influence of Temperature on the Hydroformylation of Styrene Using the Catalytic System [Pt(CH$_3$)Cl{(*S*)-MOBIPH}]/SnCl$_2$[a]

			product composition (%)					
T (°C)	*t* (h)	conversn (%)	aldehydes	ethylbenzene	polymer	*b*/*n*	op[b] (%)	config
30	240	52.7	84.6	2.5	12.9	1.09	75.8	*S*
50	164	86.7	74.7	3.7	21.6	0.73	56.3	*S*
80	17	97.8	76.9	6.6	16.5	0.77	0.1	*S*

[a] Styrene 50 mmol; [Pt(CH$_3$)Cl{(*S*)-MOBIPH}] 0.05 mmol; SnCl$_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; $P(H_2) = P(CO)$ 50 atm. [b] op = optical purity.

Table 3. Influence of Temperature on the Hydroformylation of Styrene Using the Catalytic System [Pt(CH$_3$)Cl{(*R*)-BINAP}]/SnCl$_2$[a]

			product composition (%)					
T (°C)	*t* (h)	conversn (%)	aldehydes	ethylbenzene	polymer	*b*/*n*	op[b] (%)	config
30	688	33.5	62.7	3.3	34.0	0.50	58.4	*R*
50	118	79.8	84.0	3.9	12.1	0.58	41.6	*R*
80	40	93.4	66.5	4.9	28.6	0.64	3.9	*R*

[a] Styrene 50 mmol; [Pt(CH$_3$)Cl{(*R*)-BINAP}] 0.05 mmol; SnCl$_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; $P(H_2) = P(CO)$ 50 atm. [b] op = optical purity.

Table 4. Influence of Temperature on the Hydroformylation of Styrene Using the Catalytic System [Pt(CH$_3$)Cl{(*S*,*S*)-DIOP}]/SnCl$_2$[a]

			product composition (%)					
T (°C)	*t* (h)	conversn (%)	aldehydes	ethylbenzene	polymer	*b*/*n*	op[b] (%)	config
30	66	46.8	67.1	4.1	28.8	0.29	29.2	*R*
50	22	52.6	70.2	5.1	24.7	0.41	27.2	*R*
80	2	56.6	67.3	8.8	23.9	0.59	20.7	*R*

[a] Styrene 50 mmol; [Pt(CH$_3$)Cl{(*S*,*S*)-DIOP}] 0.05 mmol; SnCl$_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; $P(H_2) = P(CO)$ 50 atm. [b] op = optical purity.

reaction rate, the regioselectivity, the optical purity, and even the absolute configuration of the branched aldehyde are greatly affected by the solvent. It is interesting to note that in toluene and tetrahydrofuran the catalyst gives 2-phenylpropanal with prevailing (*R*) configuration and a branched/normal ratio (b/n) of ~0.6, while in acetone and dichloromethane the (*S*) branched aldehyde prevails and the isomeric ratio is close to 1.

To the best of our knowledge, a similar behavior has not been reported in literature.[6a] It is likely to be connected to the particular nature of the atropisomeric BINAP ligand rather than to the nature of the platinum complex itself. In fact, experiments not reported in the tables and carried out using the DIOP containing complex **3** demonstrate that the branched aldehyde produced in dichloromethane has the same (*R*) configuration of that formed in toluene.

Even if several studies have shown that the regio- and the enantioselectivity of the platinum-catalyzed asymmetric hydroformylation can be very sensitive to the nature of the solvent,[6a] it is difficult to account for the behavior of complex **2**.

Since toluene gives the highest reaction rate and the best enantioselectivity, it was used as routine solvent for all subsequent investigations.

The data relevant to the effect of the temperature on the catalytic activity of the systems **1**/SnCl$_2$, **2**/SnCl$_2$, and **3**/SnCl$_2$ are reported in Tables 2−4, respectively.

The chemoselectivity and the regioselectivity of the reaction show only little variations over the temperature range used. As usual, on lowering the temperature the enantioselectivity improves at the expense of the reaction rate. Accordingly, when working with complex **2** at 30 °C a good optical purity is obtained, but exceedingly long reaction times are necessary to get reasonable yields (Table 3). At variance, at 30 °C complex **1** still displays a fairly good catalytic activity accompanied by an excellent optical purity (Table 2). When complexes **1** and **2** are used at 80 °C, the enantioselectivity decreases to values very close to zero, as previously found with the dichloro analogues [PtCl$_2${(*S*)-MOBIPH}][10] and [PtCl$_2${(*S*)-BINAP}][9] and some other Pt(II) catalytic precursors.[17,18]

Complex **3** displays the highest activity regardless of the reaction temperature, however the optical purity of the branched aldehyde reaches at most 30% (Table 4).

Owing to the above reported results, we deemed that only complexes **1** and **2** were worth further investigation.

The effect of the hydrogen partial pressure on the catalytic activity of complexes **1** and **2** is reported in Tables 5 and 6, respectively. With both catalysts, an increase of $P(H_2)$ produces moderate effects concerning all the main features of the reaction: (i) the hydroformylation rate is enhanced; (ii) the hydrogenation of the substrate to ethylbenzene is also enhanced though the chemoselectivity of the reaction is not greatly affected; (iii) the branched/normal isomeric ratio and the enantioselectivity are scarcely affected.

Summing up, an increase of $P(H_2)$ favorably affects the reaction as usually observed with platinum-based catalysts.[6a,b]

The data showing the influence of the CO partial pressure on the catalytic activity of complexes **1** and **2** are reported in Tables 7 and 8, respectively. With both complexes an increase of P(CO) produces several useful effects: (i) the hydroformylation rate is enhanced. It is worth noting that if the yield in aldehydes per hour

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Table 5. Influence of $P(H_2)$ on the Hydroformylation of Styrene Using the Catalytic System $[Pt(CH_3)Cl\{(S)\text{-MOBIPH}\}]/SnCl_2$[a]

			product composition (%)					
$P(H_2)$ (bar)	t (h)	conversn (%)	aldehydes	ethylbenzene	polymer	b/n	op[b] (%)	config
20	164	56.3	58.8	2.0	39.2	0.79	54.0	*S*
50	164	86.7	74.7	3.7	21.6	0.73	56.3	*S*
80	82	66.5	73.4	5.3	21.3	0.75	60.2	*S*
110	87	100	73.2	7.1	19.7	0.92	58.5	*S*

[a] Styrene 50 mmol; $[Pt(CH_3)Cl\{(S)\text{-MOBIPH}\}]$ 0.05 mmol; $SnCl_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; P(CO) 50 atm; T 50 °C. [b] op = optical purity.

Table 6. Influence of $P(H_2)$ on the Hydroformylation of Styrene Using the Catalytic System $[Pt(CH_3)Cl\{(R)\text{-BINAP}\}]/SnCl_2$[a]

			product composition (%)					
$P(H_2)$ (bar)	t (h)	conversn (%)	aldehydes	ethylbenzene	polymer	b/n	op[b] (%)	config
50	118	79.8	84.0	3.9	12.1	0.58	41.6	*R*
110	88	82.7	75.2	11.9	12.9	0.75	48.4	*R*

[a] Styrene 50 mmol; $[Pt(CH_3)Cl\{(R)\text{-BINAP}\}]$ 0.05 mmol; $SnCl_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; P(CO) 50 atm; T 50 °C. [b] op = optical purity.

Table 7. Influence of P(CO) on the Hydroformylation of Styrene Using the Catalytic System $[Pt(CH_3)Cl\{(S)\text{-MOBIPH}\}]/SnCl_2$[a]

			product composition (%)					
P(CO) (bar)	t (h)	conversn (%)	aldehydes	ethylbenzene	polymer	b/n	op[b] (%)	config
20	148	70.0	68.4	8.6	23.0	0.79	28.8	*S*
50	139	86.7	74.7	3.7	21.6	0.73	56.3	*S*
80	65	60.7	69.7	2.0	28.3	0.86	67.1	*S*
110	74	74.5	70.7	1.6	27.7	0.96	72.1	*S*

[a] Styrene 50 mmol; $[Pt(CH_3)Cl\{(S)\text{-MOBIPH}\}]$ 0.05 mmol; $SnCl_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; $P(H_2)$ 50 atm; T 50 °C. [b] op = optical purity.

Table 8. Influence of P(CO) on the Hydroformylation of Styrene Using the Catalytic System $[Pt(CH_3)Cl\{(R)\text{-BINAP}\}]/SnCl_2$[a]

			product composition (%)					
P(CO) (bar)	t (h)	conversn (%)	aldehydes	ethylbenzene	polymer	b/n	op[b] (%)	config
20	132	75.5	80.0	8.2	11.8	0.50	23.1	*R*
50	118	79.8	84.0	3.9	12.1	0.58	41.6	*R*
80	104	81.9	87.1	2.3	10.6	0.63	55.2	*R*
110	88	77.7	84.8	2.2	13.0	0.72	66.8	*R*

[a] Styrene 50 mmol; $[Pt(CH_3)Cl\{(R)\text{-BINAP}\}]$ 0.05 mmol; $SnCl_2$ 0.05 mmol; substrate/catalyst 1000/1; toluene 35 mL; $P(H_2)$ 50 atm; T 50 °C. [b] op = optical purity.

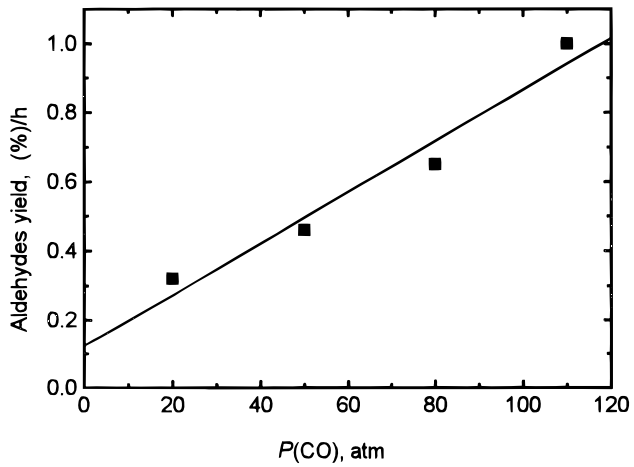

Figure 2. Influence of P(CO) on the hydroformylation rate in the presence of complex **1**.

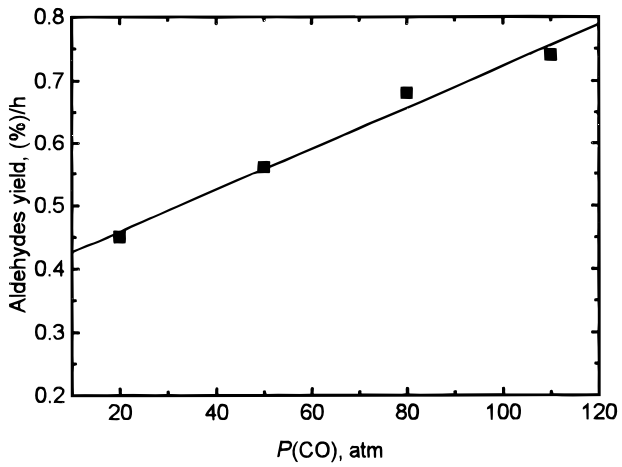

Figure 3. Influence of P(CO) on the hydroformylation rate in the presence of complex **2**.

is plotted vs P(CO), a linear trend is recognized (Figures 2 and 3); (ii) the chemoselectivity is affected to a very little extent; (iii) the regioselectivity improves; (iv) the optical purity of the branched aldehyde increases.

Indeed, the influence of P(CO) on the enantioselectivity of the reaction is impressive: the optical purity almost triples over the P(CO) range we used. A plot of the optical purity of the branched aldehyde vs P(CO) is reported in Figure 4.

The influence of P(CO) on the catalytic activity of **1** and **2** strongly resembles that observed in the case of the dichloro complex $[PtCl_2\{(S)\text{-MOBIPH}\}]$.[6] As we

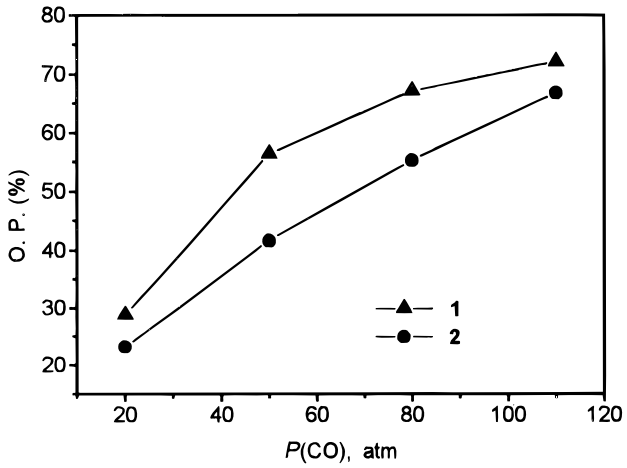

Figure 4. Influence of *P*(CO) on the optical purity of 2-phenylpropanal in the presence of complexes **1** and **2**.

Scheme 2

have outlined in the Introduction, this behavior is remarkable and deserves some comment since usually with platinum catalysts both the hydroformylation rate and the enantioselectivity are unaffected or decrease with increasing *P*(CO).[6a] Such negative influence has been attributed to the existence of different catalytic species, each one having its own activity and enantioselectivity.[19] In our opinion, to account for the data of Tables 5−8, it is not necessary to invoke the presence of different catalysts. As a matter of fact, the positive influence of $P(H_2)$ on the reaction rate has been already reported[16,20] and indicates that the rate-determining step of the reaction is the hydrogenolysis of an acyl complex as depicted in Scheme 2.

In keeping with Scheme 2, a positive effect of *P*(CO) on the reaction rate suggests that over the pressure range we have investigated [Pt−COR] is dependent on *P*(CO). Such dependence can account for the enhancement of the enantioselectivity of the reaction observed with increasing *P*(CO). The competitive pathways that produce the two enantiomeric branched aldehydes are reported in Scheme 3.

Using very high *P*(CO), the Pt−alkyl complexes are rapidly converted into the corresponding Pt−acyl complexes. These latter are then hydrogenated to give the final aldehydes. Accordingly, under high *P*(CO), the diastereomeric Pt−alkyls have little probability to interconvert and the enantioselectivity of the reaction is likely to be determined by the difference in the activation energy of the processes that lead to the formation of the two diastereomeric Pt−alkyl complexes; that is, the enantioselectivity of the reaction is kinetically controlled. To the contrary, at low *P*(CO) values, the carbonylation is slower and the concentration of the diastereomeric Pt−alkyl species likely increases. Owing to the reversibility of the insertion of an olefin into a Pt−H bond of Pt(II)−trichlorostannate complexes,[11,21] the possibility of interconversion of the diastereomers increases and the enantioselectivity of the reaction is likely to be determined by the difference in the thermodynamic stability of the two diastereomeric Pt−alkyl intermediates.[22] If this latter is smaller than the difference in the activation energies that lead to the formation of the two diastereomeric Pt−alkyl complexes, the enantioselectivity at low *P*(CO) will be lower than that at high *P*(CO).

Study of Model Reactions. To substantiate our mechanistic proposal we studied the carbonylation of complexes **1** and **2** in the presence of $SnCl_2$. The study was carried out using dichloromethane as the solvent owing to the low solubility of complexes **1** and **2** in toluene.

The reaction of **1** or **2** with $SnCl_2$ in dichloromethane (or dichloromethane-d_2) affords the corresponding trichlorostannate complexes [Pt(CH_3)($SnCl_3$){(*S*)-MOBIPH}] (**4**) or [Pt(CH_3)($SnCl_3$){(*R*)-BINAP}] (**5**). These species have been characterized in solution by low-temperature ^1H and ^{31}P NMR spectroscopies since at room temperature their spectra are dynamic owing to the equilibria involving the trichlorostannate moiety.[23] The relevant data (see Experimental Section) are in keeping with the proposed structures and agree with those of similar complexes.[11,24]

Upon treatment with 1 atm of carbon monoxide, complex **4** reacts to form two new Pt(II) species as indicated by IR and NMR spectroscopies (Scheme 4).

The most abundant species is the cationic alkyl complex [Pt(CH_3)(CO){(*S*)-MOBIPH}]$^+$[$SnCl_3$]$^-$ (**6**), definitely identified since its spectroscopic data closely match those of an authentic sample of [Pt(CH_3)(CO){(*S*)-MOBIPH}]$^+$[BF_4]$^-$ (**6a**) synthesized by reacting **1** with $AgBF_4$ under CO (Scheme 5), as described in the Experimental Section.

The formation of a second Pt(II) species is confirmed by the ^1H NMR spectrum of the solution obtained from the carbonylation reaction which shows, along with the signals stemming from complex **6**, a singlet at 1.93 ppm which can be attributed to a $COCH_3$ moiety.[25] In keeping, the IR spectrum displays a broad absorption of medium intensity at 1625 cm^{-1} attributable to the C−O stretching of an acetyl group of the type Pt-$COCH_3$.[11,26,27] Finally, the low-temperature (198 K) $^{31}P\{^1H\}$ NMR data allowed us to formulate the second species formed in the carbonylation of **4** as the acyl complex [Pt($COCH_3$)($SnCl_3$){(*S*)-MOBIPH}] (**7**) (see Experimental Section for the relevant data).

It is important to point out that the carbonylation reaction occurs in two stages since the formation of the cationic species **6** takes place in a few minutes, while

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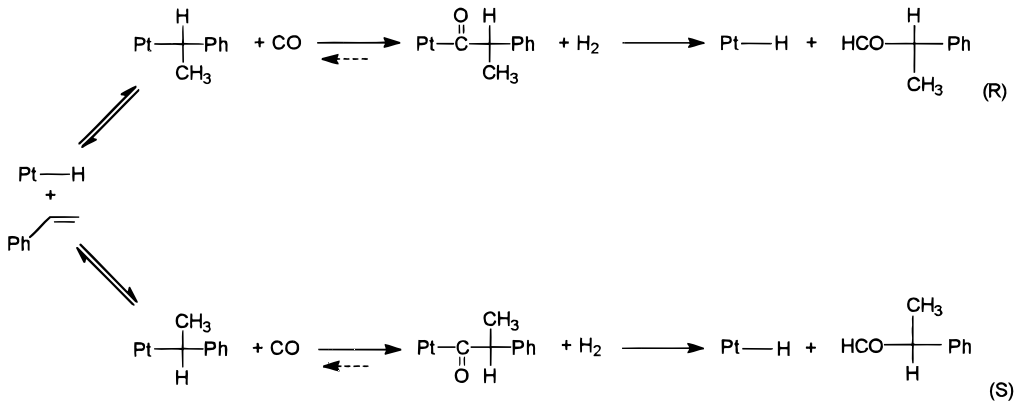
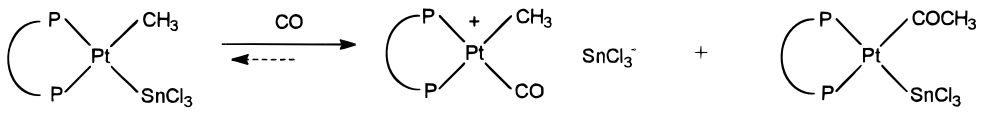
(27) In ref 24 the ν(CO) for the acetyl moiety of [Pt($COCH_3$)(CO){(*S,S*)-BDPP}]$^+$[$SnCl_3$]$^-$ is reported to be ~1710 cm^{-1}; the conflict with our data is to be attributed to the use of ^{13}C-enriched CO by Toth and co-workers.

Scheme 3



Scheme 4



4: P-P = (S)-MOBIPH
5: P-P = (R)-BINAP

6: P-P = (S)-MOBIPH
8: P-P = (R)-BINAP

7: P-P = (S)-MOBIPH
9: P-P = (R)-BINAP

Scheme 5

1 P-P = (S)-MOBIPH
2 P-P = (R)-BINAP

6a P-P = (S)-MOBIPH
8a P-P = (R)-BINAP

the formation of the acyl species **7** requires some hours. At room temperature, the relative concentration of **6** and **7** is 1.4/1, respectively, as it can be readily established by integration of the resonances relevant to the methyl groups in the ^{1}H NMR spectrum. The formation of both complexes **6** and **7** is reversible, and complex **4** can be restored by passing an argon or nitrogen stream throughout the solution.

The carbonylation of complex **5** proceeds in a strictly analogous way forming the cationic alkyl complex $[Pt(CH_3)(CO)\{(R)\text{-BINAP}\}]^+[SnCl_3]^-$ (**8**) and the neutral acyl complex $[Pt(COCH_3)(SnCl_3)\{(R)\text{-BINAP}\}]$ (**9**) in a 1/1 relative ratio. As in the case of **6**, the formulation of **8** is supported by the comparison of its spectral features with those of $[Pt(CH_3)(CO)\{(R)\text{-BINAP}\}]^+[BF_4]^-$ (**8a**) synthesized as described in the Experimental Section.

These findings indicate that the carbonylation of the alkyl species **4** and **5** is a slow process which does not quantitatively afford the corresponding Pt−acyl complexes. Probably, high CO pressures are necessary to speed up and drive the reaction to completion. IR-based studies at variable *P*(CO) and temperature are currently in progress to gain a deeper insight into carbonylation equilibria. The reluctance of complexes **4** and **5** to undergo CO insertion gives some support to our mechanistic rationalization on the influence of *P*(CO). However, taking into account that the model reactions have been studied in dichloromethane (due to the low solubility of **4** and **5** in toluene), no absolute conclusions can be drawn.

It is worth noting that the carbonylation of $[Pt(CH_3)(SnCl_3)\{(S,S)\text{-BDPP}\}]$ ((*S*,*S*)-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane), recently reported by Toth,[24] proceeds in a similar way: first a cationic carbonyl species of formulation $[Pt(CH_3)(CO)\{(S,S)\text{-BDPP}\}]^+[SnCl_3]^-$ is rapidly and quantitatively formed and then slow CO insertion takes place to give a mixture of $[Pt(CH_3)(CO)\{(S,S)\text{-BDPP}\}]^+[SnCl_3]^-$ and of the cationic acyl species $[Pt(COCH_3)(CO)\{(S,S)\text{-BDPP}\}]^+[SnCl_3]^-$. The main difference is that in our case the acyl species has to be formulated as $[Pt(COCH_3)(SnCl_3)(\text{diphosphine})]$ rather than $[Pt(COCH_3)(CO)(\text{diphosphine})]^+[SnCl_3]^-$. This difference is likely due to the fact that our model reactions were carried out under 1 atm of CO while Toth performed his investigations using *P*(CO) = 25 atm.

The carbonylation of Pt(II) complexes containing monodentate phosphine ligands has been extensively investigated.[28−30] In particular, the carbonylation of complexes of the type $[Pt(Ph)(SnCl_3)P_2]$ (P = PPh_3 or $PMePh_2$) was studied by Anderson.[30] These authors demonstrated that the presence of the trichlorostannate ligand favors a nondissociative route which allows a rapid and quantitative formation of the corresponding Pt−benzoyl complexes. Moreover, they showed that the reaction can be easily reversed in absence of CO.

The carbonylation of Pt(II)−alkyl species containing chelating diphosphine ligands has received less attention. Anderson, who studied the carbonylation of a series of complexes of the type $[Pt(Ph)Cl(P{-}Y)]$[31] (P−Y = chelating ligand), observed that the carbonylation does not take place at all when P−Y is 1,2-bis(diphenylphosphino)ethane while it proceeds smoothly to afford quantitatively the acyl complex $[Pt(COPh)Cl(P{-}Y)]$ when P−Y is 1,3-bis(diphenylphosphino)propane.

Our previous studies on the carbonylation of *cis* Pt(II)−alkyl species containing diphosphine ligands were stimulated by the interest in the role played by

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$SnCl_2$ in the Pt-catalyzed hydroformylation of olefins.[11] We observed that at atmospheric pressure the carbonylation of complexes of the type $[Pt(C_2H_5)(SnCl_3)(P-P)]$ (P−P = 1,3-bis(diphenylphosphino)propane or 1,4-bis(diphenylphosphino)butane) affords quantitatively and very rapidly the corresponding *cis* Pt−acyl complexes $[Pt(COC_2H_5)(SnCl_3)(P-P)]$.[11] Therefore, it appears that the nature of the ancillary ligands strongly influences the course of the carbonylation reaction. It should be deduced that the behavior of **4** and **5** cannot be attributed to the peculiar nature of the atropisomeric ligands we employed. Since the same behavior is observed with ligands having different basicity and which give rise to chelate rings of different size,[24] the factors that set the course of the insertion of CO are not clear.

Conclusions

The present work demonstrates that complexes of the type $[Pt(CH_3)Cl(chelating\ diphosphine)]$ in the presence of $SnCl_2$ are effective catalysts for the hydroformylation of olefins. Their catalytic activity and their chemo-, regio-, and enantioselectivity do not differ substantially from those of the corresponding dichloro species. As far as the enantioselectivity of the reaction is concerned, both the atropisomeric ligands we tested allow one to obtain good to excellent results. Unfortunately, these catalysts do not provide any improvement on the regioselectivity of the reaction which, as in the case of most of the Pt(II)-based catalysts, is disappointing since the main product is the undesired linear aldehyde.

The results of our investigations emphasize the role played by the diphosphine ligands: their nature influences not only the enantioselectivity but also the overall course of the reaction. In particular it becomes clear that when atropisomeric ligands such as BINAP are used, the process becomes very sensitive to the nature of the solvent.

Experimental Section

All the operations were carried out under argon in Schlenk-type glassware. Commercial solvents (Carlo Erba) were purified following methods described in the literature.[32]

$AgBF_4$ and anhydrous $SnCl_2$ were commercial products (Fluka). $CDCl_3$ and CD_2Cl_2 were purchased from Aldrich. The chiral ligands (*S*)-MOBIPH,[33] (*R*)-BINAP,[34] (*S*,*S*)-DIOP,[35] and complex $[Pt(CH_3)Cl(1,5\text{-}COD)]$[14] were synthesized by literature methods. ^1H and $^{31}P\{^1H\}$ NMR were obtained on a Bruker AC 200 spectrometer operating at 200.13 and 81.01 MHz, respectively. ^{31}P NMR chemical shifts are reported with positive values downfield from 85% H_3PO_4. IR spectra were registered on a Nicolet 750 FT-IR interferometer.

Elemental analyses were carried out by the Department of Organic Chemistry of the University of Florence. GC analyses were carried out on a Hewlett-Packard 5830 II series gascromatograph. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.

Hydroformylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume ∼150 mL). In a typical experiment, the reactor was charged with styrene (5.8 mL, 50 mmol), toluene (35 mL), Pt complex (0.05 mmol), and $SnCl_2$ (0.05 mmol). The reactor was flushed with nitrogen and then pressurized with H_2 and CO. The reactor was maintained at the desired temperature (±1 °C) by circulating a thermostatic fluid. At the end of the reaction, the residual gases were vented off and the composition of the raw reaction mixture was determined by GC. The branched aldehyde was isolated from the reaction mixture by distillation under reduced pressure, and its optical purity was determined by polarimetry using the specific rotatory power values reported by Consiglio.[16]

$[Pt(CH_3)Cl\{$(*S*)-MOBIPH$\}]$ (1). A dichloromethane solution of (*S*)-MOBIPH (584 mg, 1 mmol in 10 mL) was added dropwise to a dichloromethane solution of $[Pt(CH_3)Cl(1,5\text{-}COD)]$ (354 mg, 1 mmol in 20 mL). The resulting solution was stirred for 3 h under argon. Addition of *n*-hexane afforded the product as a white precipitate that was collected, washed with *n*-hexane, and dried in vacuo (yield: 650 mg, 78 %). Anal. Calcd for $C_{39}H_{35}ClO_2P_2Pt$: C, 56.56; H, 4.26. Found: C, 56.73; H, 4.34. IR spectrum (Nujol mull, CsI windows): 298 cm^{-1} (w, Pt−Cl). ^{31}P NMR ($CDCl_3$, 298 K): 17.32 (d, $J(P-P) = 17$ Hz, $J(Pt-P) = 4437$ Hz), 22.71 ppm (d, $J(Pt-P) = 1758$ Hz). ^1H NMR ($CDCl_3$, 298 K): 0.54 (dd, 3H, $J(H-P_{cis}) = 4.0$ Hz; $J(H-P_{trans}) = 7.5$ Hz, $J(H-Pt) = 56$ Hz), 3.42 (s, 3H), 3.49 (s, 3H), 6.2−8.0 ppm (m, 26 H).

$[Pt(CH_3)Cl\{$(*R*)-BINAP$\}]$ (2). Complex **2** was prepared according to the method used for the (*S*)-MOBIPH analogue (yield: 720 mg, 83%). Anal. Calcd for $C_{45}H_{35}ClP_2Pt$: C, 62.25; H, 4.06. Found: C, 62.52; H, 3.98. IR spectrum (Nujol mull, CsI windows): 300 cm^{-1} (w, Pt−Cl). ^{31}P NMR spectrum ($CDCl_3$, 298 K): 23.69 (d, $J(P-P) = 17$ Hz, $J(Pt-P) = 1760$ Hz), 18.06 ppm (d, $J(Pt-P) = 4380$ Hz). ^1H NMR: 0.33 (dd, 3 H, $J(H-P_{cis}) = 4.1$ Hz, $J(H-P_{trans}) = 7.5$ Hz, $J(H-Pt) = 57$ Hz), 6.5−8.0 ppm (m, 32 H).

$[Pt(CH_3)Cl\{$(*S*,*S*)-DIOP$\}]$ (3). Complex **3** was synthesized similarly to the (*S*)-MOBIPH analogue (yield: 560 mg, 75%). Anal. Calcd for $C_{32}H_{35}ClO_2P_2Pt$: C, 51.65; H, 4.74. Found: C, 51.77; H, 4.64. IR spectrum (Nujol mull, CsI windows): 298 cm^{-1} (w, Pt−Cl). ^{31}P NMR spectrum ($CDCl_3$, 298 K): 9.75 (d, $J(P-P) = 14$ Hz, $J(Pt-P) = 1683$ Hz), 6.80 ppm (d, $J(Pt-P) = 4340$ Hz). ^1H NMR: 0.54 (dd, 3 H, $J(H-P_{cis}) = 4.9$ Hz, $J(H-P_{trans}) = 7.3$ Hz, $J(H-Pt) = 55$ Hz), 1.16 (s, 6 H), 2.50 (m, 2 H), 3.15 (m, 2 H), 3.88 (m, 2 H), 6.40−7.40 ppm (m, 20 H).

$[Pt(CH_3)(SnCl_3)\{$(*S*)-MOBIPH$\}]$ (4). A 33 mg sample of **1** (0.04 mmol) was stirred in dichloromethane (or dichloromethane-d_2) with an equimolecular amount of anhydrous $SnCl_2$ (8 mg) until a clear yellow solution formed (∼1−2 h). ^{31}P NMR (CD_2Cl_2, 203 K): 24.63 (P *trans* to $SnCl_3$, d, $J(P-P) = 22$ Hz, $J(P-Pt) = 3707$ Hz, $J(P-^{117,119}Sn) = 4030$, 3850 Hz), 16.23 ppm (P atom *trans* to CH_3, d, $J(P-P) = 22$ Hz, $J(P-Pt) = 1963$ Hz, $J(P-^{117,119}Sn) = 217$ Hz (average value of $J(P-^{117}Sn)$ and $J(P-^{119}Sn)$). ^1H NMR: 0.71 (t, 3 H, $J(H-P_{cis}) \approx J(H-P_{trans}) \approx 6.2$ Hz, $J(H-Pt) = 55$ Hz), 3.44 (s, 3 H), 3.49 (s, 3 H), 6.2−8.0 ppm (m, 26 H).

$[Pt(CH_3)(SnCl_3)\{$(*S*)-BINAP$\}]$ (5). A 34 mg sample of **2** (0.04 mmol) was stirred in dichloromethane (or dichloromethane-d_2) with an equimolecular amount of anhydrous $SnCl_2$ (8 mg) until a clear yellow solution formed (∼1−2 h). ^{31}P NMR (CD_2Cl_2, 203 K): 25.58 (P *trans* to $SnCl_3$, d, $J(P-P) = 21$ Hz, $J(P-Pt) = 3702$ Hz, $J(P-^{117,119}Sn) = 4047$, 3869 Hz), 17.13 ppm (P *trans* to CH_3, d, $J(P-Pt) = 1986$ Hz, $J(P-^{117,119}Sn) = 215$ Hz (average value of $J(P_x-^{117}Sn)$ and $J(P_x-^{119}Sn)$). ^1H NMR: 0.50 (t, $J(H-P_{cis}) \approx J(H-P_{trans}) \approx 6.0$ Hz, $J(H-Pt) = 57$ Hz), 6.40−7.40 ppm (m, 20 H).

$[Pt(CH_3)CO\{$(*S*)-MOBIPH$\}]^+[SnCl_3]^-$ (6). IR spectrum (CH_2Cl_2, NaCl windows): 2114 cm^{-1} (s, C−O). ^{31}P NMR (CD_2Cl_2, 198 K): 18.30 (P *trans* to CO, d, $J(P-P) = 27$ Hz, $J(P-Pt) = 3316$ Hz), 14.35 ppm (P *trans* to CH_3, d, $J(P-Pt) = 1721$ Hz). ^1H NMR (298 K): 0.75 (t, Pt−CH_3, $J(H-P_{cis}) \approx J(H-P_{trans}) \approx 6.0$ Hz, $J(Pt-H) = 55$ Hz), 3.34 (s, OCH_3), 3.37 (s, OCH_3), 6.2−8.0 ppm (aromatics).

$[Pt(COCH_3)(SnCl_3)\{$(*S*)-MOBIPH$\}]$ (7). IR spectrum

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(CH_2Cl_2, NaCl windows): 1625 cm^{-1} (m, C−O). ^{31}P NMR (CD_2Cl_2, 198 K): 8.56 (P *trans* to $SnCl_3$, d, J(P−P) = 28 Hz, J(P−Pt) = 4400 Hz, $J(P-^{117,119}Sn)$ = 3217, 3078 Hz), 7.44 ppm (P *trans* to $COCH_3$, d, J(P−Pt) = 1637 Hz, $J(P-^{117,119}Sn)$ = 285 Hz (average value of $J(P-^{117}Sn)$ and $J(P-^{119}Sn)$). ^1H NMR (298 K): 1.93 (s, $COCH_3$), 3.39 (s, OCH_3), 3.42 (s, OCH_3), 6.2−8.0 ppm (m, aromatics).

[Pt(CH₃)CO{(*S*)-BINAP}]⁺[SnCl₃]⁻ (8). IR spectrum (CH_2Cl_2, NaCl windows): 2113 cm^{-1} (s, C−O). ^{31}P NMR (CD_2Cl_2, 198 K): 18.68 (P *trans* to CO, d, J(P−P) = 27 Hz, J(P−Pt) = 3329 Hz), 15.81 ppm (P *trans* to CH_3, d, J(P−Pt) = 1735 Hz). ^1H NMR (298 K): 0.71 (t, Pt−CH_3, $J(H-P_{cis}) \approx J(H-P_{trans}) \approx$ 6.0 Hz, $J(H-^{195}Pt)$ = 57 Hz), 6.3−8.0 ppm (m, aromatics).

[Pt(COCH₃)(SnCl₃){(*R*)-BINAP}] (9). IR spectrum (CH_2Cl_2, NaCl windows):1634 cm^{-1} (m, C−O). ^{31}P NMR (CD_2Cl_2, 198 K): 12.50 (P *trans* to $SnCl_3$, d, J(P−P) = 26 Hz, J(P−Pt) = 3941 Hz, $J(P-^{117,119}Sn)$ = 4100, 3920 Hz), 8.03 ppm (P *trans* to $COCH_3$, d, J(P−Pt) = 1659 Hz, $J(P-^{117,119}Sn)$ = 289 Hz (average value of $J(P-^{117}Sn)$ and $J(P-^{119}Sn)$). ^1H NMR (298 K): 2.02 ppm (s, $COCH_3$).

[Pt(CH₃)CO{(*S*)-MOBIPH}]⁺[BF₄]⁻ (6a). Under a CO atmosphere, a methanol solution of $AgBF_4$ (35 mg, 0.18 mmol in 5 mL) was added to a dichloromethane solution of [Pt(CH_3)-Cl{(*S*)-MOBIPH}] (**1**) (150 mg, 0.18 mmol in 20 mL). A white precipitate was immediately formed. The suspension was then stirred for 1 h. Treatment of the suspension with activated charcoal and filtration gave a clear solution which was concentrated under reduced pressure. Addition of diethyl ether afforded **6a** as an off-white powder (yield: 130 mg, 80%). Anal. Calcd for $C_{40}H_{35}O_3P_2BF_4Pt$: C, 52.94; H, 3.89. Found: C, 53.02; H, 3.91. IR spectrum (CH_2Cl_2, NaCl windows): 2114 cm^{-1} (s, C−O). ^{31}P NMR ($CDCl_3$, 298 K): 18.34 (d, J(P−P) = 27 Hz, J(P−Pt) = 3360 Hz), 14.56 ppm (d, J(P−Pt) = 1713 Hz). ^1H NMR: 0.83 (t, $J(H-P_{cis}) \approx J(H-P_{trans})$ = 6.0 Hz, J(H−Pt) = 55 Hz), 3.34 (s, 3 H), 3.38 (s, 3 H), 6.3−8.0 ppm (m, 26 H).

[Pt(CH₃)CO{(*S*)-BINAP}]⁺[BF₄]⁻ (8a). Complex **8a** was synthesized in a 80% yield similarly to complex **6a**. Anal. Calcd for $C_{46}H_{35}OP_2BF_4Pt$: C, 58.30; H, 3.72. Found: C, 58.14; H, 3.66. IR spectrum (CH_2Cl_2, NaCl windows): 2113 cm^{-1} (s, C−O). ^{31}P NMR ($CDCl_3$, 298 K): 18.82 (d, J(P−P) = 27 Hz, J(P−Pt) = 3371 Hz), 16.80 ppm (d, J(P−Pt) = 1720 Hz). ^1H NMR: 0.73 (t, $J(H-P_{cis}) \approx J(H-P_{trans})$ = 6.0 Hz, J(Pt−H) = 57 Hz), 6.2−8.0 ppm (m, 32 H).

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