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AN EVALUATION OF THE P^{IV}=S REDUCTION—COMPLEXATION BY NICKELOCENE AS A SYNTHETIC TOOL IN ORGANOPHOSPHORUS CHEMISTRY; TOWARDS THE SYNTHESIS OF FUNCTIONAL PHOSPHINES WITH AN OPTICALLY ACTIVE PHOSPHORUS CENTRE *

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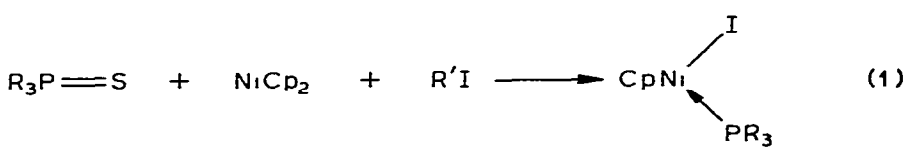
Summary

Metalation of $PhP(S)Me_2$ by BuLi followed by reaction with carbonyl derivatives afforded functional and chiral phosphine sulfides of general formula $PhP(S)(Me)CH_2Z$ with Z = $Ph_2C(OH)$, PhC(O), HC(O), COOEt, with Ph_2CO [Z = $Ph_2C(OH)$] a bifunctional compound $PhP(S)(CH_2Z)_2$ was also obtained These sulfides were reduced to the corresponding phosphines L through their CpNi(I)L complexes by treatment with nickelocene and allyl iodide followed by decomplexation with $P(OMe)_3$. The synthesis of the phosphinoacetaldehyde is especially noteworthy. Use of an optically active phosphine sulfide showed that this reduction—complexation—decomplexation procedure proceeded with full retention of configuration at phosphorus Thus, it is possible to synthesize functional phosphines with an optically active phosphorus centre. The synthesis of two optically active nickelocenes $[R^*C_5H_4]_2Ni$ is described When treated with a phosphine sulfide LS they yielded the corresponding optically active $[R^*C_5H_4]Ni(I)L$ complexes When L was chiral, attempted separation of the diastereoisomeric complexes failed.

The reduction—complexation of phosphine sulfides by nickelocene [1,2] depicted by eq 1 can be viewed as the first step of a new procedure for reducing



(1)

R = CH_3 , C_3H_5

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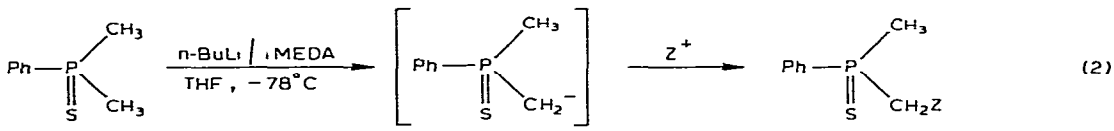
P^{IV}=S compounds to the corresponding P^{III} derivatives. The classical procedures (Na, NaH, Fe, Ni, $LiAlH_4$, Si_2Cl_6, see ref (3)) often need drastic conditions and are not compatible with sensitive functional groups In the proposed procedure, however, the exceptional ability of P^{III} compounds to give nickel complexes acts as a powerful driving force for the reduction and thus allows use of mild conditions and selectivity

A growing interest in functional phosphines as ligands for transition metals [4—6] is obvious in the literature, for example, it has been shown recently that phosphinoacetates can act as labile bidentate ligands with Rh and Ir [6].

In view of the above we decided to extend our investigations of the nickelocene reduction—complexation of phosphine sulfides considered as a synthetic tool in organophosphorus chemistry and chose as an underlying theme the synthesis of functional phosphines with optically active phosphorus centres, these molecules are obviously interesting for asymmetric catalysis

(A) Synthesis of chiral and functional phosphine sulfides

We chose phenyldimethylphosphine sulfide I as the starting point This sulfide was metalated by n-BuLi in THF at low temperature and then reacted with various organic reagents to afford functional sulfides (eq 2) During the syn-

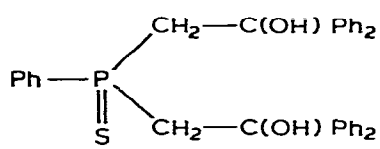


(2)

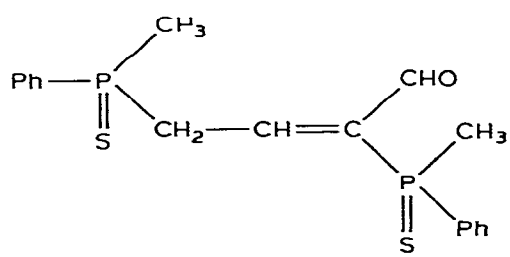
(I)

Z^+ =				
Ph_2CO	II, Z =	$Ph_2C(OH)$	70%
PhCOOEt	III Z =	PhC(O)	50%
PhCN	III, Z =	PhC(O)	90%
HCOOEt	IV Z =	HC(O),	42%
$CO(OEt)_2$	V Z =	COOEt,	40%

thesis of alcohol II the diol VI is always obtained as a byproduct. The best yield of VI (45%) was achieved when using 2 equivalents of n-BuLi and Ph_2CO for 1 equivalent of I. A similar phenomenon was observed when studying the metalation of 1-phenyl-3,4-dimethylphosphol-3-ene sulfide [7]; in the latter case, however, the two α positions were allylic and gave no suspicion of the generality of this type of bicondensation, the origin of which remains obscure (ketyl radical anions are perhaps involved). On the other hand, a limited crotonization of aldehyde IV always takes place during its synthesis leading to VII (yield ~8%).



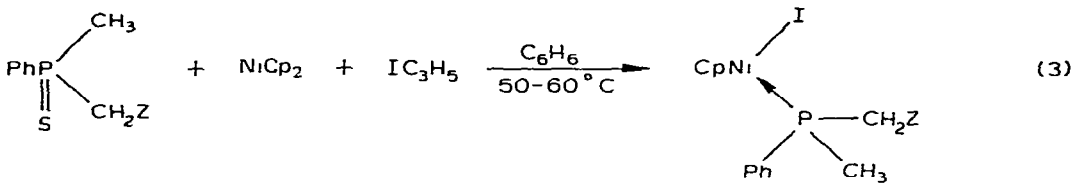
(VI)



(VII)

(B) Synthesis of chiral and functional phosphines by reduction—complexation

The functional sulfides II—V were treated with nickelocene and allyl iodide to give the corresponding complexes (eq 3) The compatibility of the reduction

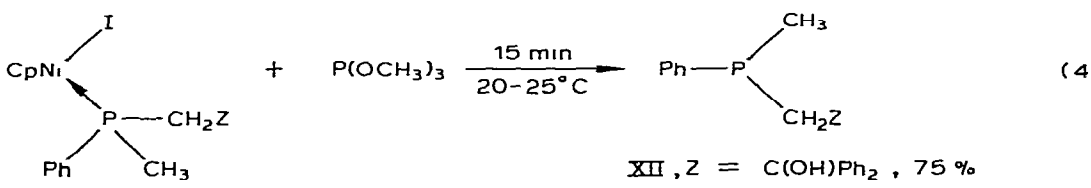


(3)

VIII, Z = C(OH)Ph$_2$, 76 %
IX, Z = C(O)Ph, 70 %
X Z = CHO, 52 %
XI, Z = COOEt, 80 %

complexation with such sensitive functions as an aldehyde group is especially noteworthy The diol VI, however, does not give any complex when using the same conditions; this is a perfect illustration of the adverse effect of steric bulk at phosphorus on this reaction and is in line with the observations of Tolman on the relative stabilities of nickel—P^{III} complexes [8]

In a previous paper [2] we proposed two methods for decomplexing the phosphines L from their CpNi(I)L complexes The first involved the clean displacement of L by P(OMe)$_3$ Unfortunately, an excess of P(OMe)$_3$ reacted with CpNi(I)[P(OMe)$_3$] to give IMe as a by-product, thus L was quaternized after its decomplexation To avoid this drawback a method relying upon the destruction of the nickel complex by cyanide ion in alcohol was proposed In the present work this method was found to be incompatible with carbonyl groups. Thus, we reverted to the first method, by limiting the excess of P(OMe)$_3$ and the reaction time a clean decomplexation was obtained and quaternization was avoided (eq 4). Owing to its instability the aldehyde XIV was converted "in situ" into



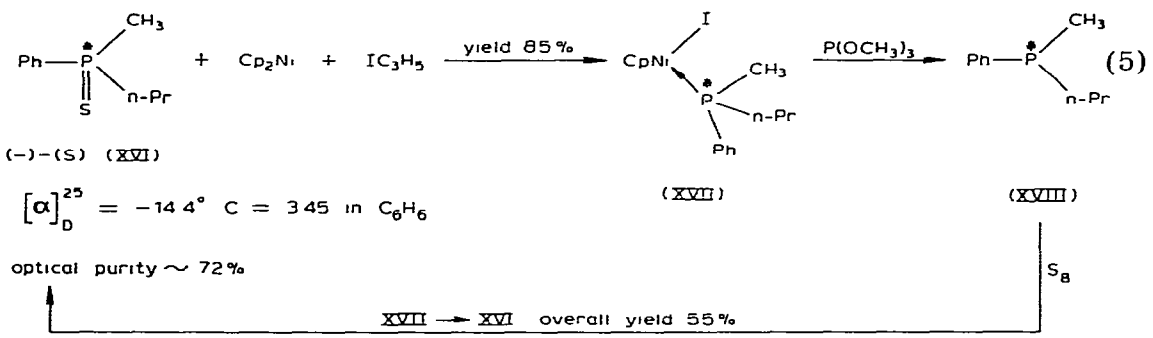
(4)

XII, Z = C(OH)Ph$_2$, 75 %
XIII Z = C(O)Ph, 40 %
XIV, Z = CHO, 60 %
XV, Z = COOEt, 75 %

its P-sulfide which was purified and characterized as usual Monitoring the reaction on TLC sheets showed that complex X was completely destroyed by P(OMe)$_3$ within 5 min at room temperature; the aldehyde XIV gave a reducing spot on silica gel at $R_f \sim 0.21$ (C_6H_6/CH_3COOEt 90/10). Remembering that the first phosphinoaldehyde, i e , diphenylphosphinoacetaldehyde, was described in 1977 [9] as a very unstable oil, the compatibility of this method with sensitive functional groups is thus firmly established.

(C) Reduction—complexation and optical activity at phosphorus

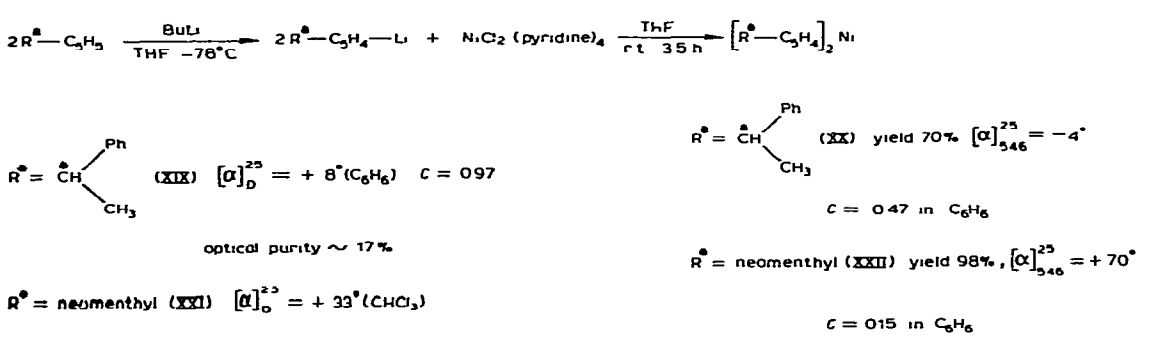
Optically active methylphenylpropylphosphine sulfide XVI was prepared by the method of Mislow [10] This sulfide was subjected to the nickelocene reduction—complexation. The deep red colour of the resulting complex XVII was too strong for its rotation to be measured Thus it was destroyed directly by reaction with $P(OMe)_3$ and the resulting phosphine XVIII was reacted in situ with sulfur to reform the starting sulfide XVI The optical purity of XVI was the same before and after the reduction—complexation, decomplexation, sulfurization procedure (see eq 5) Since the reactions of phosphines with sulfur are



known to proceed with complete retention [11], our result establishes that the coupled reduction—complexation and decomplexation by $P(OMe)_3$ proceeds with full retention

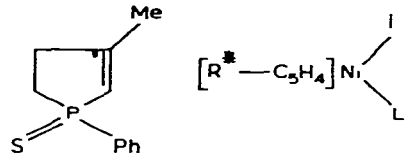
(D) Towards the synthesis of functional phosphines with optically active phosphorus

Mislow has shown that α-metalation does not destroy the P optical activity of a phosphine oxide [12]; very probably the same result holds true for phosphine sulfides. Thus, starting with a non-functional optically active phosphine sulfide, it is possible to graft a functional group as described in (A) and then to reduce the P=S bond as described in (B) while keeping the optical activity as proven in (C). This approach will be described elsewhere. Hereafter another tentative approach is described in which advantage was taken of the reduction—complexation step for introducing optical activity at phosphorus The initial step was the preparation of optically active nickelocenes XX and XXII by means of reaction 6.

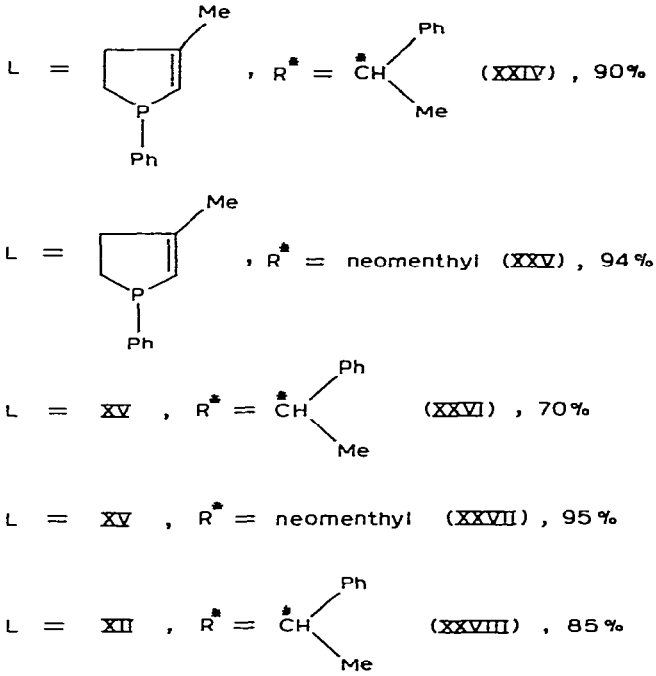


As far as we know XX and XXII are the first optically active nickelocenes described in the literature The starting cyclopentadienes XIX and XXI were prepared as described in refs. 13 and 14

Nickelocenes XX and XXII were reacted with allyl iodide and sulfides II, V and XXIII in the usual way The reduction—complexation succeeded and complexes XXIV—XXVIII were obtained in good yields Each of these complexes



(XXIII)



was a 50/50 mixture of two diastereoisomers and the decomplexation of these mixtures afforded the corresponding phosphines with no optical activity Every attempt at separating these diastereoisomers by chromatographic methods failed It was not even possible to distinguish clearly these isomers from their NMR spectra except when the coordinated phosphine was the most bulky and dissymmetric of the series i e. XII in complex XXVIII The ^{1}H NMR spectrum of XXVIII showed P—Me groups at 0 95 (^2J(H—P) 9 Hz) and 0 98 (^2J(H—P) 9 Hz) ppm and C(H)Me groups at 1.48 (^3J(H—H) 7 Hz) and 1.53 (^3J(H—H) 7 Hz) ppm Similarly, the ^{31}P NMR spectrum showed peaks at 8 04 and 8 41 ppm Nevertheless, the separation failed. These experiments demonstrate that reduction—complexation of phosphine sulfides also takes place with bulkily substituted nickelocenes Thus it is possible to synthesize optically active [R*—C_5H_4]Ni(I)L complexes which are potentially interesting (e g in asymmetric catalysis). However, because of the failure of the separation step, this approach is useless for the purposes of this article

(E) Experimental

Chromatographic separations were performed on silica gel columns (70-230 mesh MERCK) under argon when necessary. The spectroscopic features of some

of the compounds described in this work are collected in Table I The spectra of the other compounds were recorded in the same way as stated in the Table

(i) Preparation of chiral and functional sulfides

To a solution of 3 4 g (0 020 mol) of dimethylphenylphosphine sulfide I in 50 ml of THF and 10 ml of TMEDA at −78° C is added dropwise 10 ml of a solution of n-BuLi 2 *N* in hexane (0.020 mol) The temperature is allowed to rise to 25° C. After 1 h of stirring 0 022 mol of the appropriate reagent in 15 ml of THF is added at −20° C. Stirring is continued for 3 h at room temperature The solution is then cooled, treated with 15 ml H_2O and acidified with 2 *N* hydrochloric acid The aqueous solution is extracted with diethyl ether, dried over sodium sulfate and evaporated. The different products are isolated as follows

Methylphenyl[2-diphenyl-2-hydroxyethyl]phosphine sulfide, II The volatile materials are removed by distillation (Kugelrohr) at 120° C (0 15 mmHg) The residual oil is chromatographed using C_6H_6/AcOEt 90/10 as eluent to give 5 g of alcohol II (R_f 0 4) which is recrystallized from ether (m p 152° C) and 1 2 g of diol VI (R_f 0.47) which is recrystallized from CH_2Cl_2/Et_2O (1/4) (m p 177° C)

Phenylbis[2-diphenyl-2-hydroxyethyl]phosphine sulfide, VI Similarly, with two equivalents of n-BuLi and Ph_2CO the alcohol II is obtained in 40% yield and diol VI in 45% yield. VI. ^{1}H NMR ($CDCl_3$), δ 3 02 (d, ^2J(H—P) 10 Hz, 4 H, CH_2P), 5.85 (s, 2 H, OH); 6 90—7.30 (m, 25 H, Ph) ppm I R (Nujol), ν(OH) 3340 and 3370 cm^{-1}.

Methylphenylphenacylphosphine sulfide, III The sulfide I is removed by Kugelrohr distillation and the crude sulfide III chromatographed (C_6H_6 eluent)

Methylphenyl[formylmethyl]phosphine sulfide, IV and 1-formylbis[1,3-phenylmethylphosphine sulfide] propene, VII After evaporation of the solvent the crude oil is chromatographed (eluent C_6H_6/AcOEt 90/10) to give the aldehyde IV (R_f 0.27) and the aldol product VII (R_f 0.2). VII ^{1}H NMR ($CDCl_3$), δ 2.03 (d, ^2J(H—P) 12.5 Hz, 3 H, P—C<u>H</u>$_3$), 2.16 and 2.17 (2d, ^2J(H—P) 14 Hz, 3 H, P—C<u>H</u>$_3$, two isomers *Z* and *E*), 3.50 and 3.65 (2d, ^2J(H—P) 15 Hz, 2 H, P—C<u>H</u>$_2$); 9.66 and 9.71 (2d, ^2J(H—P) 16.3 Hz and 16 1 Hz, 1 H, CHO) ppm IR (pure), ν(C=O) 1677 cm^{-1}. δ ^{31}P ($CDCl_3$), +52.9 ppm.

Methylphenyl[carbethoxymethyl]phosphine sulfide, V After Kugelrohr distillation of sulfide I, sulfide V is recrystallized from pentane m p. 52° C

(ii) Preparation of complexes CpNi(I)L

The complexes are prepared according to ref. 2. Crude complexes VIII, IX, XI and XVII are purified by chromatography with benzene. VIII, m p 172° C (C_6H_6/EtOH, 50/50), XI, m.p. 81° C (EtOH).

Complex X is prepared as above from the crude reaction mixture of sulfides I, IV and VII and chromatographed using C_6H_6/AcOEt 90/10 as eluent. R_f X ~0.5. Mass spectra: VIII, *m/e* 570—572 (*M*, 2%), 250—252 (*M* − *L*, 27%), 200 (100%). IX, *m/e* 492—494 (*M*, 3%); 250—252 (*M* − *L*, 58%); 241 (L — M, 100%). X, *m/e* 416—418 (*M*, 13%); 250—252 (*M* − *L*, 100%); 166 (L, 100%) XI, *m/e* 460—462 (*M*, 11%); 333—335 (*M* − I, 46%), 210 (L, 100%). XVII, ^{1}H NMR ($CDCl_3$), δ 1.0 (t, 3 H, $(CH_2)_2$—C<u>H</u>$_3$); 1.73 (d, ^2J(H—P) 9 5 Hz, 3 H, P—C<u>H</u>$_3$), 5.15 (s, 5 H, Cp); 7.24—7.60 (m, 5 H, Ph) ppm. δ ^{31}P (C_6D_6), +15.3 ppm. Mass spectrum, *m/e* 416—418 (*M*, 48%); 166 (L, 66%).

(iii) Preparation of functional phosphines

At room temperature 0 5 ml of $P(OMe)_3$ are added to 3×10^{-3} mol of complex dissolved in 20 ml of C_6H_6 The red solution becomes rapidly green and finally brown After stirring for 15 min the mixture is evaporated and chromatographed on a short column The phosphines XII, XIII and XV are eluted, respectively, with C_6H_6/AcOEt (90/10), C_6H_6, and C_6H_6/AcOEt (95/5) They are characterized by their ^1H and ^{31}P NMR spectra (see Table 1) and by their benzyl bromide phosphonium salts

Benzylmethylphenyl[2-diphenyl-2-hydroxyethyl]phosphonium bromide m p. 130°C ^1H NMR ($CDCl_3$), δ 1 92 (d, ^2J(H—P) 13 3 Hz, 3 H, CH_3P), 4 05—4 55 (m, 4 H, $\overset{+}{P}CH_2$), 5.77 (s, 1 H, OH), 6 90—7 33 (m, 20 H, Ph) ppm Benzyl bromide phosphonium salts of XIII and XV have already been described in the literature [15]

The benzene solution of phosphine XIV is sulfurized 'in situ' by treatment with elemental sulfur (0 5 g) at room temperature for 3 h The reaction mixture is filtered and the solvent is removed under reduced pressure to yield the crude phosphine sulfide IV which is chromatographed

(iv) Reduction—complexation of optically active (—)-(S) methylphenylpropylphophine sulfide, XVI

Complex XVII (2×10^{-3} mol) is treated as described above for IV After chromatography (C_6H_6/AcOEt 90/10) a recrystallization from pentane gives 218 mg (55%) of sulfide (—)-(S) XVI m p , 60—61°C

(v) Preparation of optically active nickelocenes

(1) Bis[(1-phenylethyl)cyclopentadienyl]nickel, XX A 2 N hexane solution (25 ml) of n-BuLi is added dropwise at —78°C to the corresponding amount of optically active (1-phenylethyl)cyclopentadiene dissolved in 100 ml of THF and prepared as described in ref 13 At the end of the addition the temperature is allowed to rise to —20°C and 0 025 mol of freshly prepared $NiCl_2$(pyridine)$_4$ is added The resulting brown-green mixture is then warmed to room temperature, stirred for 3 h and concentrated The residue is extracted with pentane, filtered and evaporated The crude oil is chromatographed using pentane/C_6H_6 as eluent to give 8 g of a deep green oil. The starting cyclopentadiene is removed by a rapid distillation (Kugelrohr) at 80°C (0 15 mmHg) and the residual oil is chromatographed again to give 7 g of the green oil XX which crystallizes on standing at —10°C (mixture of two diastereoisomers).

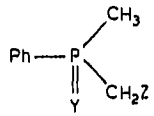
(2) Bis[neomenthylcyclopentadienyl]nickel, XXII The procedure employed is similar to that for nickelocene XXII but the pentane extract is analytically pure.

(vi) Preparation of optically active complexes

Complexes XXIV to XXVIII are prepared as above and chromatographed using C_6H_6 as eluent

XXIV: ^1H NMR ($CDCl_3$), δ 1.48 (d, ^3J(H—H) 7 Hz, 3 H, $HC(Ph)$—Me), 1 88 (s, 3 H, CH_3—C=C), 2 60 (m, 4 H, P—$(CH_2)_2$—); 3 70 (q, 1 H, Me—$C(Ph)$—H); 4 67—4.88—5 0—5.37 (m, 4 H, Cp), 5.62 (d, ^2J(H—P) 34 Hz, 1 H, =CH—P), 7 10—7.70

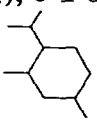
TABLE 1

SPECTRAL DATA FOR FUNCTIONAL PHOSPHINE DERIVATIVES 

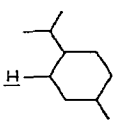
Y	Z	No	^{1}H NMR [a]				Y	Z	^{31}P NMR [b] δ	IR [c] ν	
			CH_3		CH_2						
			δ	[^2J(H–P)]	δ	[^2J(H–P)]					
S	$Ph_2C(OH)$	II	1 50	[13]	3 08	[10]	—	OH 6 26	—	OH	3280
S	PhC(O)	III	2 13	[13 6]	3 84	[15]	—	—	—	CO	1655
S	HC(O)	IV	2 03	[13]	3 33	[14 3]	—	CHO 9 56 ^3J(H–H) 3	28 7 ($CDCl_3$)	CO	1718 ($CHCl_3$)
S	COOEt	V	2 10	[13 6]	3 18	[13 5]	—	Et 1 10 (t) 4 0 (q)	—	CO	1720
CpNiI	$Ph_2C(OH)$ [d]	VIII	1 0	[9]	3 60 [e]		5 18	OH 1 35	7 9 (C_6D_6)	OH	3130
CpNiI	PhC(O) [d]	IX	1 87	[9]	4 03 [e]		5 15	—	13 1 (C_6D_6)	CO	1665
CpNiI	HC(O) [d]	X	1 84	[9]	3 47 [e]	[11 3]	5 17	CHO 9 90	8 5 (C_6D_6)	CO	1713 ($CHCl_3$)
CpNiI	COOEt [d]	XI	2 08	[9 6]	3 25	[9]	5 17	Et 1 05 (t) 3 92 (q)	11 (C_6D_6)	CO	1725
	$Ph_2C(OH)$ [f]	XII	1 08s		2 78s		—	OH 3 10	−19 ($CDCl_3$)		
	PhC(O) [f]	XIII	1 50	[5]	3 12s		—	—	−35 (C_6D_6)		
	COOEt [f]	XV	1 42	[4 3]	2 63	[2 4]	—	Et 1 05 (t) 3 90 (q)	−37 8 (C_6D_6)		

[a] δ in ppm, J in Hz, $CDCl_3$, internal TMS [b] H_3PO_4 85% as external standard δ positive for downfield shift [c] in KBr or as such except when noted ν in cm^{-1} [d] The complexes were also characterized by mass spectral analysis, in each case the molecular peak was present [e] Complex system [f] The phosphines were also characterized as their benzyl bromide salts see under Experimental

(m, 10 H, Ph) ppm δ ^{31}P ($CDCl_3$), +52 25 ppm Mass spectrum *m/e* 530—532 (*M*, 11%), 176 (L, 100%)

XXV ^{1}H NMR ($CDCl_3$), δ 1 96 (s, 3 H, C=C(CH$_3$)—), 2 65 (m, 4 H, P—(CH$_2$)$_2$—), 2 88 (broadened s, 1 H, ), 4.85—5 07—5 28 (4 H, Cp), 5 70 (d, ^2J(H—P) 33 Hz, 1 H, P—C(H)=C), 7 30—7 75 (m, 5 H, Ph) ppm δ ^{31}P (C_6D_6), +51 24 ppm Mass spectrum *m/e* 564—566 (*M*, 13%), 388—390 (*M* — L, 12%), 176 (L, 100%)

XXVI ^{1}H NMR ($CDCl_3$), δ 1 0 (t, 3 H, OCH$_2$—CH$_3$), 1 52 (d, ^3J(H—H) 7 0 Hz, 3 H, C(H)—Me), 2 05 (d, ^2J(H—P) 9 3 Hz, 3 H, P—Me), 3 25 (d, ^2J(H—P) 8 7 Hz, 2 H, P—CH$_2$), 3 88 (q, 2 H, O—CH$_2$—CH$_3$); 3 70 (m, 1 H, C(H)(Me)), 4 57—4 82—5 0—5.35 (4 H, Cp), 7 20—7 60 (m, 10 H, Ph) ppm δ ^{31}P ($CDCl_3$), + 14 47 ppm IR (pure), ν(C=O) 1720 cm^{-1} Mass spectrum. *m/e* 564—566 (*M*, 4%), 354—356 (*M* — *L*, 25%), 210 (L, 100%)

XVII. ^{1}H NMR ($CDCl_3$), δ 2.08 (d, 3 H, P—Me), 2.85 (s, 1 H, ), 3 28 (d, ^2J(H—P) 8 2 Hz, 2 H, P—CH$_2$), 3 86 (q, 2 H, O—CH$_2$—CH$_3$), 4 70—5.0—5 20 (4 H, Cp), 7 30—7 60 (5 H, Ph) ppm. δ ^{31}P (C_6D_6), +15.79 ppm. IR ($CHCl_3$) ν(C=O) 1725 cm^{-1} Mass spectrum *m/e* 598—600 (*M*, 36%), 210 (L, 100%)

XXVIII· ^{1}H NMR ($CDCl_3$), δ 0 95 and 0 98 (2 × d, ^2J(H—P) 9 Hz, 3 H, P—CH$_3$), 1.48 and 1 53 (2 × d, ^2J(H—P) 7 Hz, 3 H, C(Me)—H), 3 43—3.83—4 05 (3 × d, ^2J(H—P) 13 7, 6 5, 6 7 Hz, 2 H, P—CH$_2$), 4.45—4 92—5 40 (m, 4 H, Cp), 7.15—7 25 (m, 15 H, Ph) ppm. δ ^{31}P ($CDCl_3$), +8 04 and +8.41 ppm, 2 diastereoisomers. IR ($CHCl_3$), ν(OH) 3420 cm^{-1} Mass spectrum *m/e* 674—676 (*M*, 1%), 170 (100%)

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