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THE PREPARATION, REACTIONS AND STRUCTURE OF BIS[BIS(TRICYCLOHEXYLPHOSPHINE)NICKEL] DINITROGEN, $\{[(C_6H_{11})_3P]_2Ni\}_2N_2$

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SUMMARY

The treatment of nickel acetylacetonate with trimethylaluminium in the presence of tricyclohexylphosphine and nitrogen gives the dinitrogen complex $\{[(C_6H_{11})_3P]_2Ni\}_2N_2$ (I). Intermediate methyl–nickel complexes can be isolated, and provide an insight into the mechanism of formation of (I). The nitrogen molecule is readily displaced to give $[(C_6H_{11})_3P]_2Ni$. The reactions of this coordinatively unsaturated species are described.

The structure of the dinitrogen complex has been determined by X-ray crystallography from 5977 reflections using an automatic diffractometer, and refined anisotropically for all 80 atoms to a final *R*-value of 11%. The molecule is shown to contain a linear Ni–N–N–Ni system in which the nitrogen molecule is enclosed in a cage formed by four of the cyclohexyl rings. The N–N bond distance is 1.12 Å.

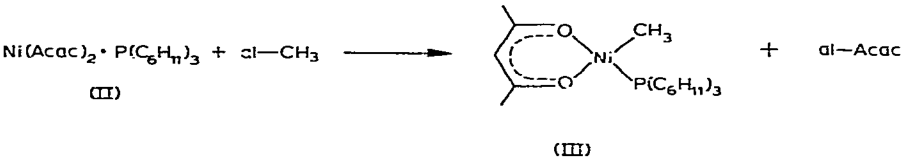
INTRODUCTION

Transition metal complexes of molecular nitrogen have received considerable attention since the discovery of the first complex in 1965, and examples have been reported for Mo, Re, Fe, Ru, Os and Ni[1-4]. Since our original communication[5,6] two further publications have appeared concerning compounds tentatively assigned as phosphine-stabilized dinitrogen nickel hydride species[7,8].

PREPARATION

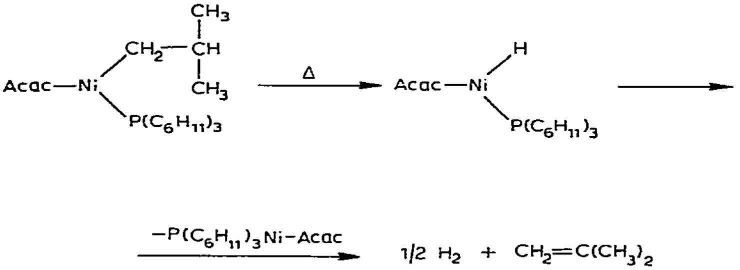
(I) may be prepared in around 50% yield by treatment of nickel acetylacetonate with trimethylaluminium in the presence of tricyclohexylphosphine and nitrogen. Isolation of the intermediates involved gives some insight into the mechanism of formation of the dinitrogen complex and also into the mechanism of the reduction of nickel acetylacetonate by trialkylaluminiums in general.

The addition of tricyclohexylphosphine to nickel acetylacetonate in toluene produces a blue-green 1/1 adduct (II). Treatment of (II) with trimethylaluminium leads to formation of (tricyclohexylphosphine)methylnickel acetylacetonate (III) as a yellow crystalline solid, soluble in ether and aromatic solvents and sparingly soluble

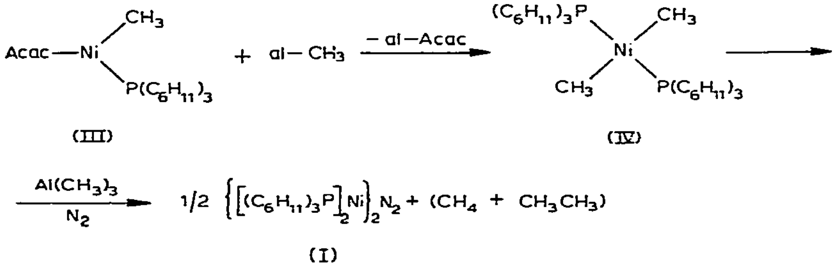


(II) (III)

in hydrocarbon solvents. The formulation of this complex as (III) is supported by its mass spectrum, and the liberation of one mole of methane on protonation with acetic acid. A high field doublet at 10.3 τ (C_6D_6) $J(PH) = 5$ Hz in the NMR spectrum is attributable to the methyl group attached to nickel while the non-equivalence of the methyl groups attached to the acetylacetonate fragment suggest that the molecule is square planar*. The ethyl and isobutyl analogues to (III) may be obtained using triethylaluminium or triisobutylaluminium as reducing agent. The isobutyl complex is thermally unstable decomposing to give a mixture of iso-butene and hydrogen: β-hydrogen transfer occurring to give an unstable nickel hydride which decomposes by homolytic cleavage:



Further treatment of (III) with trimethylaluminium in the presence of a second molecule of tricyclohexylphosphine gives bis(tricyclohexylphosphine)dimethyl nickel (IV), as a colourless solid:



(III) (IV) (I)

(IV) is only slightly soluble in aromatic solvents and is extremely light sensitive turning pink with evolution of a mixture of ethane and methane {light sensitivity has also been observed for $[(C_6H_{11})_3P]_2Ni(CH_3)H^{10}$}. The low solubility has prevented the measurement of the NMR spectrum and it is assigned a *trans* configuration by analogy with $[(o\text{-}C_6H_5C_6H_4O)_3P]_2Ni(CH_3)_2$ in which the methyl group appears as a triplet at 10.40 τ (C_6H_6)[11] (a tetrahedral arrangement is also possible but less probable).

(IV) alone does not react with nitrogen. However, in the presence of further

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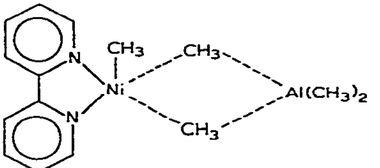
* This geometry has been confirmed[25] by an X-ray structural determination. The Ni–C-distance is 1.98 Å.

trimethylaluminium immediate reaction occurs to give the dinitrogen complex (I) with evolution of methane and ethane. Presumably an intermediate involving bridging methyl groups between the nickel and aluminium atoms is involved. This suggestion is made plausible by the recent isolation of a thermally unstable 1/1 adduct of (2,2′-bipyridine)dimethyl nickel with trimethylaluminium which is believed to have the structure (V)[12]:



(V)

The catalytic decomposition of alkylnickels in the presence of alkylaluminiums has also been studied with the complex $[(C_6H_{11})_3P]_2Ni(CH_3)H$, (VI)[10], which decomposes in the presence of trimethylaluminium eliminating methane:

$$\underset{\text{(VI)}}{[(C_6H_{11})_3P]_2Ni(CH_3)H} \xrightarrow{Al(CH_3)_3} [(C_6H_{11})_3P]_2Ni + CH_4$$

Experiments using $Al(CD_3)_3$ introduce a further subtlety: the gas evolved on reacting equimolar proportions of (VI) and $Al(CD_3)_3$ consists of 70% CD_3H and 30% CH_4, showing that *exchange* of the methyl group occurs much more rapidly than the coupling reaction[13].

Attempts to prepare the dinitrogen complex (I) using triethylaluminium results in formation of the well known bis(tricyclohexylphosphine)nickel–ethylene complex[14]. If triisobutylaluminium is used (I) is formed in reduced yield (8%). We have not been able to isolate well defined dinitrogen complexes using ligands other than tricyclohexylphosphine. However, evidence for the formation of a nitrogen complex in small yield where the ligand is triphenylphosphine, trimorpholinophosphine and triethylphosphine was obtained by treating the reaction mixture after reduction with excess olefin (cyclododecatriene) which in these cases caused nitrogen to be evolved. In the presence of tris(2-biphenylyl) phosphite no nitrogen absorption was observed and moreover $[(o\text{-}C_6H_5\text{-}C_6H_4O)_3P]_2Ni(CH_3)_2$ failed to react with trimethylaluminium at normal temperatures[11]. This may well be a result of steric hindrance by the large phosphite molecules which prevents interaction between the aluminium and the dimethylnickel group.

An alternative method for the preparation of the dinitrogen complex (I) is the displacement of the ethylene molecule in $[(C_6H_{11})_3P]_2Ni\text{-}C_2H_4$. This may be accomplished by bubbling argon or nitrogen, by means of a sinter, through a toluene solution of the ethylene complex heated to 100°. The reaction is accelerated by addition of a third molecule of the phosphine in which case the product is tris(tricyclohexylphosphine)nickel (VII) which dissociates in solution and readily absorbs nitrogen at room temperature to give (I).

$$[(C_6H_{11})_3P]_2NiC_2H_4 + P(C_6H_{11})_3 \xrightarrow[-C_2H_4]{100^\circ} \underset{\text{(VII)}}{[(C_6H_{11})_3P]_3Ni} \rightarrow$$

$$\xrightarrow[N_2]{25^\circ} \tfrac{1}{2}\{[(C_6H_{11})_3P]_2Ni\}_2N_2 + P(C_6H_{11})_3$$

STRUCTURE*

Bis[bis(tricyclohexylphosphine)nickel] dinitrogen, (I), is a dark red solid which may be recrystallized from toluene under nitrogen as needle shaped crystals, which show monoclinic symmetry, the space group being $P2_1/n$. Cell data as determined by least-squares-treatment of θ-values of 49 general reflections (diffractometer data) are given in Table 1.

The crystal structure of (I) has been determined with difficulty from 5977 reflections (Cu-$K\alpha$, $\lambda = 1.5418$ Å), collected with our standard procedure from a crystal with the dimensions 0.09 × 0.6 × 0.21 mm, sealed in a glass capillary under nitrogen. Since the Patterson map, due to the special arrangement of the heavy atoms, could not be interpreted at the start of the structure elucidation, an attempt was made to solve the structure by iterative direct methods[15]. One of the combinations (Table 2) of 8 symbolic signs gave after 5 cycles an E-map for 127 generated reflections at a probability level of 0.969, whose strongest peaks could be interpreted

TABLE 1

CELL DATA

Space group: $P2_1/n$
$a = 21.8005 \pm 0.005$ Å
$b = 16.4748 \pm 0.003$ Å
$c = 21.2713 \pm 0.005$ Å
$\beta = 103.250 \pm 0.02^\circ$
$Z = 4$
d(calcd.) = 1.12 g·cm^{-1}
d(obs.) = 1.13 g·cm^{-1}

TABLE 2

h k l	*E*	Symb. sign	Interactions	Final sign
3 2 2	3.031	A	31	−
$\bar{4}$ 1 2	3.156	B	45	+
$\bar{8}$ 4 7	2.819	C	39	+
$\bar{2}$ 3 3	2.907	D	42	−
$\bar{3}$ 6 3	3.747	E	37	+
$\overline{13}$ 5 0	3.009	F	39	+
7 9 3	3.204	G	41	+
0 0 2	3.054	H	62	−

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* C. Krüger and Y.-H. Tsay.

as the final heavy-atom-arrangement. All of the signs obtained proved to be correctly chosen. Attempts to locate all the lighter atoms, in other E-maps as well as in heavy-atom-phased Fourier-maps, failed because of the unsatisfactory ratio of heavy atoms to light atoms: Only faint images of the cyclohexyl-rings could be identified. The structure was finally resolved by the application of phase refinement in direct space[16], starting with the heavy atom framework at an R-factor of 49 %. After 8 cycles of phase refinement in which atoms below a prespecified threshold-value (20 % of the expected peak intensity) were excluded in the atoms list, no considerable improvement of the

TABLE 3

FINAL ATOMIC COORDINATES (× 1000)

Atom	x	y	z	Atom	x	y	z
P(1)	−142	186	176	C(33)	31	−122	364
P(2)	−45	118	346	C(34)	76	−115	318
P(3)	43	533	293	C(35)	54	−57	261
P(4)	157	385	230	C(36)	33	25	282
N(1)	−12	278	261	C(37)	−27	527	328
N(2)	21	331	262	C(38)	−85	489	281
Ni(1)	−65	196	261	C(39)	−144	480	309
Ni(2)	73	415	261	C(40)	−127	428	370
C(1)	−138	259	108	C(41)	−73	467	419
C(2)	−78	241	84	C(42)	−13	476	390
C(3)	−68	305	34	C(43)	102	588	357
C(4)	−68	392	59	C(44)	78	657	393
C(5)	−127	408	83	C(45)	129	686	452
C(6)	−136	347	135	C(46)	194	704	436
C(7)	−154	91	126	C(47)	215	630	402
C(8)	−92	43	136	C(48)	165	608	339
C(9)	−101	−26	85	C(49)	21	611	227
C(10)	−147	−89	98	C(50)	1	566	161
C(11)	−208	−36	86	C(51)	−8	628	105
C(12)	−201	28	140	C(52)	−53	698	112
C(13)	−220	205	194	C(53)	−30	739	177
C(14)	−274	232	137	C(54)	−23	682	236
C(15)	−337	240	162	C(55)	230	386	298
C(16)	−333	296	221	C(56)	213	370	363
C(17)	−276	274	274	C(57)	267	388	421
C(18)	−215	265	249	C(58)	324	339	412
C(19)	−113	95	383	C(59)	342	353	347
C(20)	−159	39	337	C(60)	287	338	288
C(21)	−220	43	360	C(61)	178	450	164
C(22)	−214	10	423	C(62)	185	538	187
C(23)	−170	69	468	C(63)	189	596	131
C(24)	−105	63	452	C(64)	242	568	101
C(25)	15	161	418	C(65)	235	480	80
C(26)	−12	241	436	C(66)	234	425	136
C(27)	35	280	495	C(67)	157	285	190
C(28)	98	294	476	C(68)	104	282	128
C(29)	127	213	461	C(69)	103	198	94
C(30)	81	171	405	C(70)	95	130	141
C(31)	−10	17	331	C(71)	147	130	203
C(32)	17	−39	389	C(72)	147	215	239

TABLE 4

FINAL THERMAL PARAMETERS (× 1000)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
P(1)	73	55	79	−10	9	−23
P(2)	55	42	86	−2	−1	4
P(3)	61	43	83	−9	3	−10
P(4)	68	49	98	4	6	0
N(1)	19	38	104	−30	25	9
N(2)	15	36	100	−16	22	5
Ni(1)	60	53	86	−4	13	−15
Ni(2)	54	43	97	0	8	2
C(1)	79	63	53	−6	14	1
C(2)	46	100	120	−0	24	30
C(3)	101	60	94	−15	9	23
C(4)	107	68	97	−4	−2	0
C(5)	69	83	104	12	−5	1
C(6)	91	67	65	2	23	2
C(7)	75	77	182	23	−33	4
C(8)	128	95	170	24	−82	−8
C(9)	197	98	239	25	−28	101
C(10)	205	54	420	1	52	133
C(11)	131	103	263	−5	−80	3
C(12)	226	127	371	−118	−158	175
C(13)	26	121	107	31	−5	14
C(14)	28	90	167	27	−0	−37
C(15)	48	138	174	13	−3	−51
C(16)	108	97	149	−19	−40	0
C(17)	76	146	110	18	−14	0
C(18)	134	140	102	33	−18	64
C(19)	63	93	86	−55	11	13
C(20)	68	107	227	−77	−66	33
C(21)	141	278	164	−117	2	16
C(22)	120	294	156	−196	−0	20
C(23)	182	449	200	−214	−72	95
C(24)	162	230	129	−69	52	24
C(25)	72	61	78	−24	−17	−29
C(26)	83	62	105	17	−42	−14
C(27)	78	139	101	−44	−63	10
C(28)	91	101	88	−24	−5	1
C(29)	65	87	90	−39	−28	−59
C(30)	45	73	150	−9	4	−5
C(31)	103	45	119	18	−1	10
C(32)	108	35	147	43	42	−12
C(33)	134	48	183	5	36	48
C(34)	115	80	175	6	36	20
C(35)	164	50	176	32	−27	38
C(36)	87	80	99	10	−24	37
C(37)	35	69	94	−13	−15	11
C(38)	47	58	117	2	3	−7
C(39)	15	111	124	−15	−3	34
C(40)	83	92	139	−17	19	22
C(41)	76	97	122	−14	−7	23
C(42)	90	100	56	−22	45	4

(Continued)

TABLE 4 (*continued*)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
C(43)	106	52	88	−7	−72	5
C(44)	104	69	104	−28	−33	11
C(45)	138	96	120	−22	−54	−8
C(46)	99	113	193	−35	−41	69
C(47)	68	147	137	−39	−63	−4
C(48)	49	235	177	−73	−101	51
C(49)	128	37	63	−6	7	−4
C(50)	152	75	83	29	15	40
C(51)	171	94	71	20	63	31
C(52)	126	82	148	57	12	−2
C(53)	167	41	130	31	25	−10
C(54)	99	18	134	40	17	16
C(55)	40	110	113	1	39	2
C(56)	121	144	113	30	36	1
C(57)	130	149	101	35	−29	−89
C(58)	101	202	171	50	30	−27
C(59)	84	177	148	18	30	18
C(60)	35	71	160	44	−4	−18
C(61)	101	67	114	0	19	70
C(62)	181	61	127	−42	8	68
C(63)	118	83	111	−29	5	33
C(64)	118	101	140	−57	−9	49
C(65)	142	155	176	59	54	94
C(66)	148	112	101	30	66	78
C(67)	107	70	97	4	−4	18
C(68)	89	74	112	2	−37	−37
C(69)	112	0	0	0	0	0
C(70)	132	0	0	0	0	0
C(71)	101	0	0	0	0	0
C(72)	122	0	0	0	0	0

R-factor (39%) was achieved. At this stage, from 82 peaks, 72 carbon atoms and 2 nitrogen atoms proved to be in logical positions from the chemical evidence.

Isotropic least-squares refinement of the atoms as found resulted after 7 cycles in an *R*-factor of 19.4%. Changing to anisotropic refinement for 6 cycles for all atoms gave a final *R*-factor of 11.3%. The refinement was stopped at this stage because the new chemical information obtained was not comparable to the computing efforts involved. The final atomic coordinates with their thermal parameters are listed in Tables 3 and 4.

DISCUSSION OF THE STRUCTURE

The structure as found (Fig. 1) is in accordance with the chemical evidence. The most notable feature of the structure seems to be the steric arrangement of the four tricyclohexylphosphine groups. The framework of the $\begin{smallmatrix}\mathrm{P}\\ \mathrm{P}\end{smallmatrix}\!\!>\!\mathrm{Ni}$ groups has a dihedral angle of 105°, thus the linearly end-on bonded nitrogen is surrounded in a cage-like arrangement of cyclohexyl rings. This fact, which is clearly shown in Fig. 2,

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* A list of the structure factors may be obtained from the authors on request.

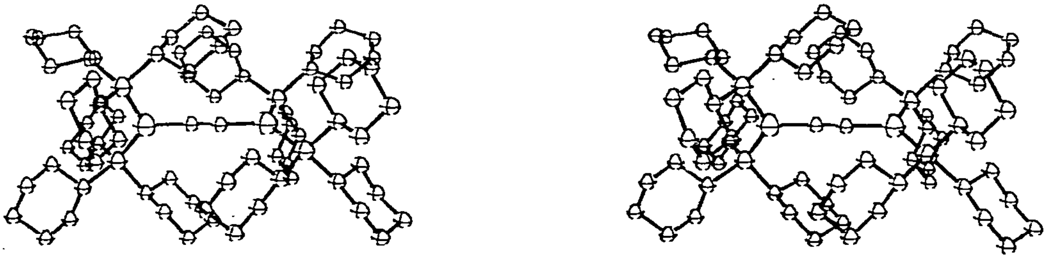


Fig. 1. Stereoscopic view of the molecule

seems to be the main reason for the stability of the complex.

The nickel atoms have an exactly planar trigonal-bipyramidal (or pseudo five-coordinated trigonal-bipyramidal) geometry, with somewhat distorted bonding angles to the phosphorus atoms. (Figs. 3, 4) This is probably due to steric repulsion of the bulky ligands. It is noteworthy that this distortion is symmetrical only around one of the nickel atoms.

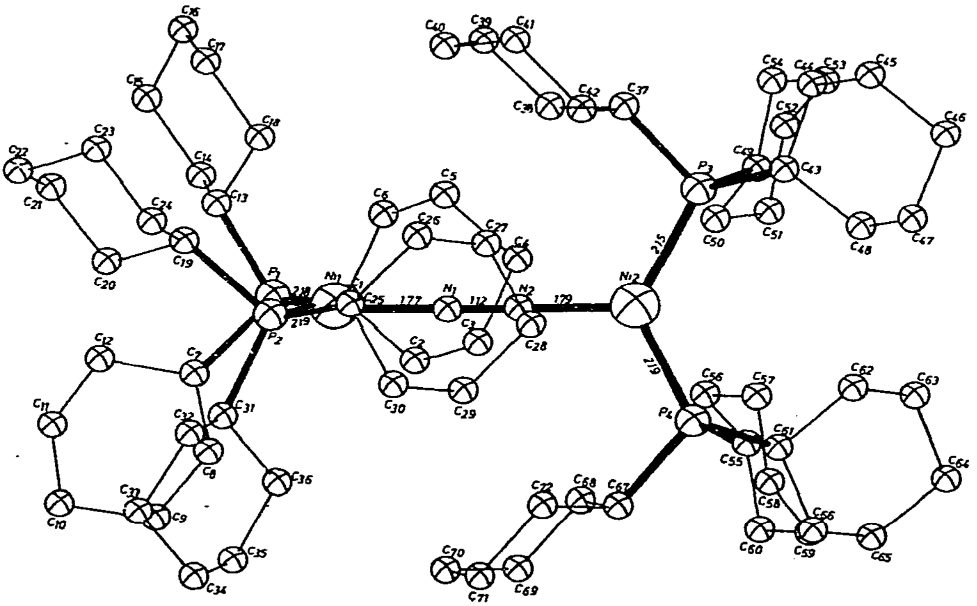


Fig. 2.

The distance within the linearly bonded nitrogen is, as expected, slightly longer than in free nitrogen (1.0976 Å) and compares well with other known distances in related compounds (1.12–1.16 Å)[17]; however, there is no additional lenghtening due to the bis-coordination of the nitrogen. The Ni–N bonds are symmetrical within experimental errors. The structure obtained is consistent with the predicted geometry for this class of compounds for which a bonding scheme similar to that found in metal carbonyls has been proposed[2,18,19]. The phosphorus atoms of the ligands form distorted tetrahedra with average C–P–Ni angles of 115.4° and average P–C distances of 1.884 Å. The latter distances compare well to those in similar phosphines and phosphine complexes.

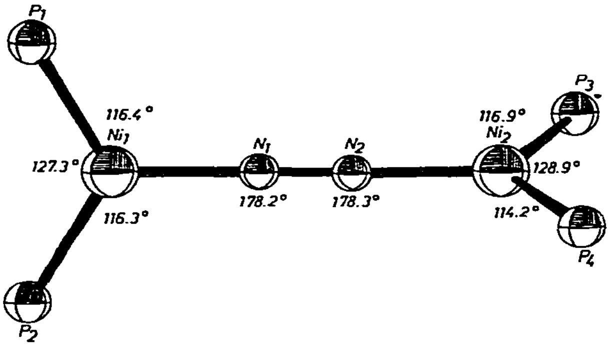


Fig. 3.

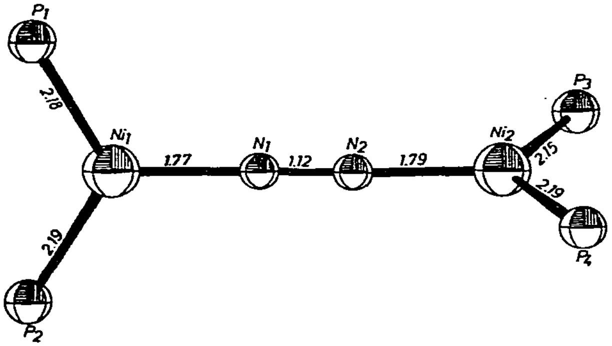


Fig. 4.

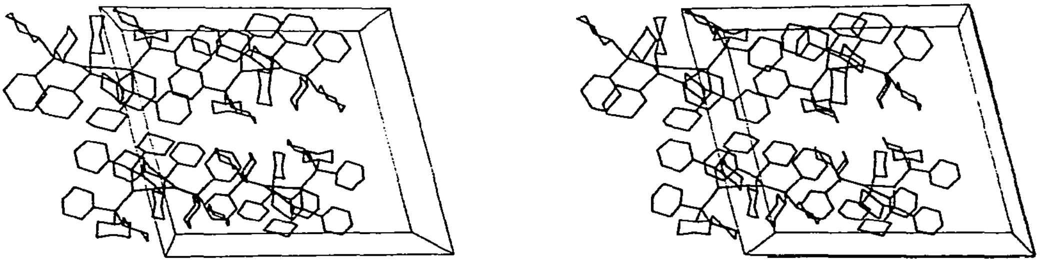


Fig. 5. Stereoscopic view of a unit cell content, viewed along *b*; the *a* axis is horizontal.

All cyclohexyl rings are in the chair conformation; the averaged C–C distance is 1.538 Å, the average bond angles are 108.7°. The pseudo-symmetry of the system is destroyed by the arrangement of just one ring, this is probably due to packing forces (Fig. 2).

REACTIONS

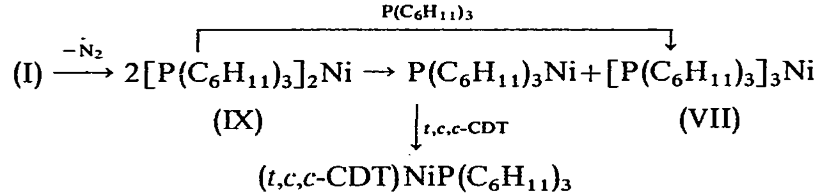
A cryoscopic molecular weight determination in benzene shows that (I) is dissociated in solution (mol.wt. found: 675; calcd.: 1266) which also accounts for the observation of a band at 2028 cm^{-1} (toluene) in the IR spectrum which is attributable to the N–N stretching frequency of [bis(tricyclohexylphosphine)nickel] dinitrogen, (VIII).

$$\underset{\text{(I)}}{\{[(C_6H_{11})_3P]_2Ni\}_2N_2} \rightarrow \underset{\text{(VIII)}}{[(C_6H_{11})_3P]_2NiN_2} + \underset{\text{(IX)}}{[(C_6H_{11})_3P]_2Ni}$$

This band disappears if argon is bubbled through a solution of the dinitrogen complex or if it is subjected to a vacuum and reappears on resaturation of the solution with nitrogen. The nitrogen molecule from (I) is readily displaced by olefins and the reaction with cyclododecatriene (CDT) has been used to determine the nitrogen in (I); exactly $\frac{1}{2}$ mole of nitrogen per g-atom of nickel is evolved with simultaneous formation of bis(tricyclohexylphosphine) nickel–CDT[20].

$$\text{(I)} + 2\,\text{CDT} \rightarrow 2\,[(C_6H_{11})_3P]_2Ni\text{–}CDT + N_2$$

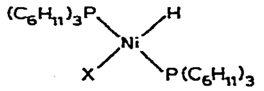
Evaporation of a toluene solution of (I) to dryness followed by trituration with pentane gives bright violet crystals of tris(tricyclohexylphosphine)nickel (VII) and a mono(tricyclohexylphosphine)nickel species is left as a pale yellow pentane solution. This mono-phosphine complex could not be isolated but its presence has been verified by trapping as its *trans,cis,cis*-CDT derivative[20]. (VII) can be prepared in quantitative yield by addition of one mole of phosphine to (IX).



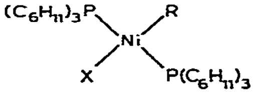
$$\begin{tikzcd}[column sep=small]
\text{(I)} \arrow[r, "-N_2"] & 2[P(C_6H_{11})_3]_2Ni \arrow[r] \arrow[rrr, bend left, "P(C_6H_{11})_3"] & P(C_6H_{11})_3Ni \arrow[d, "t,c,c\text{-CDT}"] & + & {[P(C_6H_{11})_3]_3Ni} \\
 & \text{(IX)} & (t,c,c\text{-CDT})NiP(C_6H_{11})_3 & & \text{(VII)}
\end{tikzcd}$$

In common with practically all the known transition metal dinitrogen complexes no reaction of (I) has been observed involving the nitrogen molecule. However, the facile displacement of the nitrogen molecule gives access to the coordinatively unsaturated bis(tricyclohexylphosphine)nickel complex (IX) in solution. Although the chemistry of coordinatively unsaturated palladium and platinum complexes has received some attention[21,22] the inaccessibility of such complexes of nickel has, until recently[23], prevented their investigation. We have already reported[10] some of the more important reactions of (IX) and will briefly discuss further reactions here.

(IX) undergoes oxidative addition with acidic compounds (*e.g.* HCl or phenol) to give a nickel hydride complex[10], (X), or with alkyl halides (*e.g.* methyl iodide or ethyl bromide) to give a nickel alkyl complex, (XI).

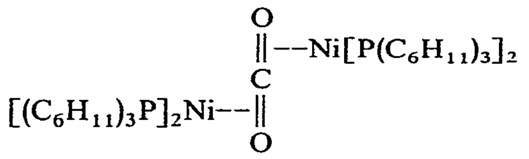


(X)



(XI)

Carbon dioxide forms a dinickel complex in which both C=O groups are bonded to nickel, (XII) (a linear Ni–OCO–Ni structure cannot be excluded).



$$\begin{array}{l} \qquad\qquad\quad O \\ \qquad\qquad\quad \|\text{--}Ni[P(C_6H_{11})_3]_2 \\ \qquad\qquad\quad C \\ [(C_6H_{11})_3P]_2Ni\text{--}\| \\ \qquad\qquad\quad O \end{array}$$

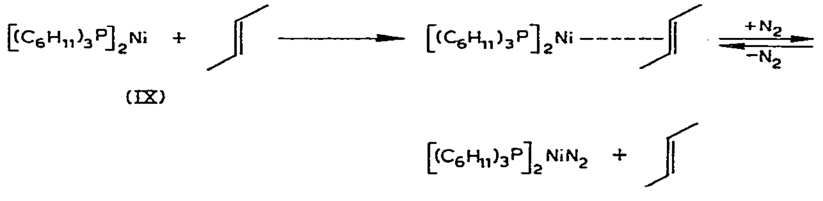
(XII)

$[(C_6H_5\text{-}o\text{-}C_6H_4O)_3P]_2NiP(C_6H_{11})_3$

(XIII)

Phosphine or phosphite molecules also readily react. The product being controlled by both electronic and steric considerations. For example reactions with tris(2-biphenylyl)phosphite (a ligand of comparable size with tricyclohexylphosphine) gives the bis(phosphite)nickel–phosphine complex, (XIII)[23]. The reaction being controlled by the favourable combination of two electron accepting ligands opposed to one predominantly electron donating ligand.

Reactions of (IX) with olefins occur quantitatively and smoothly to give nickel–olefin complexes. Cyclohexene, and *cis*- or *trans*-butene readily form olefin complexes with (IX), without isomerization of the last two olefins occurring [this is in contrast to the result of the reaction of nickel acetylacetonate with triisobutylaluminium in the presence of two equivalents of tricyclohexylphosphine and *cis*- or *trans*-butene which leads in both cases to bis(tricyclohexylphosphine)nickel–1-butene[24]]. The lability of the bond between these olefins and nickel is illustrated by the partial displacement of the olefin by nitrogen in aromatic solvents. No olefin complex could be isolated from the reaction of tetramethylethylene with (IX).



EXPERIMENTAL

All experiments were carried out under pure argon. Solvents were rendered water and oxygen free by distillation from sodium–potassium alloy. Absolute nitrogen was obtained by passing normal laboratory nitrogen through $Al(C_2H_5)_2OC_2H_5$. Nickel values were obtained by titration against titriplex. ^1H NMR spectra were recorded with a Varian A-60 spectrometer with TMS as internal standard. Volumes of liberated gases are corrected to NTP.

Preparation of bis[bis(tricyclohexylphosphine)nickel] dinitrogen, (I)

(*a*). *By reduction.* To a mixture of 5 g (~20 mmoles) of nickel acetylacetonate and 12 g (~40 mmoles) of tricyclohexylphosphine in 35 ml of toluene cooled to −20°, was slowly added 2.2 ml of $Al(CH_3)_3$ in 5 ml of toluene while at the same time bubbling nitrogen into the reaction mixture. The reactants were allowed to slowly reach room temperature and then stirred for a further 15 h. Dark red crystals of (I) precipitated. Solvent was removed by filtration and the crystals washed with ether (3 × 10 ml) (yield 5.8 g, 46 %). The product so obtained is analytically pure but may be recrystallized from toluene under nitrogen to give dark glistening needles (Found: Ni, 9.4. $C_{72}H_{132}N_2Ni_2P_4$ calcd.: 9.3 %.) Nitrogen determination: 0.654 g of (I) was dissolved in 10 ml of benzene and cooled to −78°. 1 ml of CDT was added and the mixture allowed to reach room temperature. 11.8 ml (calcd. 11.6 ml) of gas was evolved and shown mass spectrometrically to consist of pure nitrogen.

(*b*). *From ethylene bis(tricyclohexylphosphine)nickel*[14]. A solution of 20.4 g (31.5 mmoles) of ethylene bis(tricyclohexylphosphine)nickel and 8.8 g (31.5 mmoles) of tricyclohexylphosphine was prepared in 1.5 l of toluene. The reaction mixture was heated at 100° for 3 h while at the same time bubbling argon through the mixture by means of a glass sinter. The solution was evaporated to 100 ml and nitrogen bubbled through giving (I) (6.9 g; 34% theory).

Preparation of methyl(tricyclohexylphosphine) nickel acetylacetonate, (III)

2.5 g (10 mmoles) of nickel acetylacetonate and 2.8 g (10 mmoles) of tricyclohexylphosphine were stirred in 50 ml of ether and the mixture cooled to −40°. 0.5 ml of $Al(CH_3)_3$ in 5 ml of pentane was added slowly with stirring and the mixture allowed to reach 0°. A bright yellow precipitate of (III) was formed. Stirring was continued until the reduction was complete (ca. 3 h). The solvent was removed and the precipitate washed with ether (4 × 10 ml). Yield 3.0 g (66% theory). The product may be recrystallized with considerable loss from an ether-pentane mixture to give yellow prisms (Found: Ni, 12.8. $C_{24}H_{43}NiO_2P$ calcd.: Ni, 13.0%.) Determination of the Ni-bonded CH_3-group: 0.589 g of (III) dissolved in 20 ml of toluene was treated at −78° with 1 ml of acetic acid and allowed to reach room temperature. 28.6 ml (calcd.: 29.1 ml) of gas was evolved which was identified mass spectroscopically as methane. The mass spectrum of (III) showed nickel containing peaks at *m/e* 452 (M), 437 ($M-CH_3$), 355, 256, 241, 157. The NMR spectrum (C_6D_6) had absorptions at τ 4.72 (s, Acac-H), 8.16, 831 (s, Acac-CH_3), 8.25–9.25 (br, C_6H_{11}) and 10.32 (Ni-CH_3, d, *J* 5 Hz).

Preparation of ethyl(tricyclohexylphosphine)nickel acetylacetonate

The reaction was carried out as above for (III) except that 0.7 ml $Al(C_2H_5)_3$ was used as reducing agent and 50 ml of monoglyme was used as solvent. The resulting yellow solid was recrystallized from toluene/ether to give 2.0 g (30% theory) of the ethylnickel compound as yellow prisms (Found: Ni, 12.6. $C_{25}H_{45}NiO_2P$, calcd.: Ni, 12.5%.) Determination of the ethyl group: 0.676 g of the complex gave 30 ml (calcd.: 32 ml) of gas on treatment with acetic acid which was shown mass spectroscopically to be ethane. The mass spectrum showed the following nickel containing peaks at *m/e* 437 ($M-C_2H_5$) 355, 256 and 157. The NMR spectrum (C_6D_6) had absorptions at τ 4.72 (s, Acac-H), 8.17, 8.32 (s, Acac-CH_3) 8.0–9.0 (br, C_6H_{11}, CH_3), 9.44 (t, Ni–CH_2).

Preparation of isobutyl(tricyclohexylphosphine)nickel acetylacetonate

The reaction was carried out as above for the ethyl compound exept that 1.3 ml of i-Bu_3Al was used as reducing agent. The compound was recrystallized from pentane to give 1.8 g (35% theory) of the isobutyl complex as yellow prisms (Found: Ni, 12.1. $C_{27}H_{49}NiO_2P$ calcd.: Ni, 11.9%.) Determination of the isobutyl group: 0.76 g of the complex was dissolved in 10 ml of cyclohexane and heated for 6 h at 60° to give 18.8 ml of gas which was shown mass spectrometrically to consist of 60% hydrogen and 40% isobutene. The mass spectrum showed the following nickel containing peaks at *m/e* 437 ($M-C_4H_9$), 256. The NMR spectrum (C_6D_6) had absorptions at τ 4.76 (Acac-H);

8.54, 8.65 (s, Acac-CH_3); 8.0–9.0 [br, C_6H_{11} and $CH(CH_3)_2$], 9.5 (d, Ni–CH_2).

Dimethylbis(tricyclohexylphosphine)nickel (IV)

A solution of 2.4 g of (III) and 1.5 g of the tricyclohexylphosphine in 50 ml of ether was cooled to $-40°$ and 0.34 ml of $Al(CH_3)_3$ in 5 ml of pentane added slowly with stirring. The mixture was allowed to reach room temperature and the resulting precipitate isolated and washed with ether (3 x 10 ml) to give analytically pure (IV) (2.0 g; 50% theory) (Found: Ni, 9.8. $C_{38}H_{72}NiP_2$ calcd.: Ni, 9.9%.) Determination of the methyl groups: 0.927 g of (IV) in 10 ml of toluene was treated at $-78°$ with 2 ml of acetic acid. 58 ml (calcd. 63 ml) of gas was evolved which was shown mass spectroscopically to consist exclusively of methane. (IV) turns rapidly pink in sunlight with gas evolution

Ethylbromobis(tricyclohexylphosphine)nickel (XI)

Argon was passed into a solution of 2 g of the dinitrogen complex in 50 ml of toluene. After ca. 2 h an orange solution of bis(tricyclohexylphosphine)nickel resulted. The apparatus was attached to a gas-burette and cooled to $-78°$; 0.25 ml of ethyl bromide was added and the stirred solution allowed to reach room temperature. A yellow solution was formed without gas evolution, removal of the solvent by distillation and addition of pentane (10 ml) gave yellow crystals of (XI) (Found: Ni, 8.15. $C_{38}H_{71}BrNiP_2$ calcd.: 8.1%.) *tert*-Butylchlorobis(tricyclohexylphosphine)nickel [yellow crystals (Found: Ni, 8.45. $C_{40}H_{81}ClNiP_2$ calcd.: Ni, 8.25%.) and methyliodobis(tricyclohexylphosphine)nickel (colourless crystals) were prepared similarly.

Bis[bis(tricyclohexylphosphine)nickel] carbon dioxide, (XII)

Argon was passed into a solution of 2 g of the dinitrogen complex in 50 ml of toluene until the solution was orange. The solution was evaporated to dryness and 50 ml of ether added. CO_2 was passed into the solution which turned yellow and from which yellow crystals of (XII) were obtained on cooling (Found: Ni, 8.8. $C_{73}H_{132}Ni_2P_4O_2$ calcd.: Ni, 9.1%.) CO_2 determination: 0.8624 g of (XI) were heated with 2 g of triphenyl phosphite to 80° 18 ml of gas (calcd. 15 ml) was evolved which was shown mass spectrometrically to be pure CO_2. A band at 1735 cm^{-1} (KBr) in the IR spectrum may be assigned as a CO stretching frequency.

Bis(tricyclohexylphosphine)nickel–trans-butene

Argon was bubbled into a solution of 2 g of (I) in 50 ml of toluene until the solution became orange (ca. 2 h). The solution was cooled to $-20°$ and *trans*-butene passed in until the solution temperature reached 0°. Solvent was removed and the resulting precipitate washed with pentane to give orange-yellow crystals of the *trans*-butene adduct (Found: Ni, 8.6. $C_{40}H_{74}NiP_2$ calcd.: Ni, 8.7%.) Displacement of the olefin with triphenyl phosphite and analysis of the gas showed that it consisted to 99.8% of *trans*-butene.

Bis(tricyclohexylphosphine)nickel–cis-butene

This compound was prepared similarly [yellow crystals, (Found: Ni, 8.4. $C_{40}H_{74}NiP_2$ calcd.: Ni, 8.7%.)] Displacement of the olefine with triphenyl phosphite and analysis of the gas showed that it consisted to 99.6% of *cis*-butene.

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