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STUDIES ON THE REACTIVITY OF METAL π-COMPLEXES

XII*. PREPARATIVE RESULTS AND STEREOCHEMICAL COURSE OF THE REACTIONS OF π-CYCLOPENTADIENYLNICKEL—DIOLEFIN COMPLEXES WITH THE METHOXIDE ANION

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Summary

The reactions of $[C_5H_5Ni(Diene)]BF_4$ (Diene = norbornadiene or 1,5-cyclooctadiene) with the methoxide anion OMe^- in methanol give the uncharged complexes $C_5H_5NiC_7H_8OMe$ (IV) and $C_5H_5NiC_8H_{12}OMe$ (VI), respectively. (VI) is readily converted, by abstraction of methanol, into $C_5H_5NiC_8H_{11}$ (VII) possessing a cyclic π-allylic ligand. The preparation of $C_5H_5PdC_7H_8OMe$ (V) from $[C_7H_8OMePdCl]_2$ and TlC_5H_5 is also reported. The NMR data of (IV), (V), (VI), (VII) and of the π-cyclooctadienylpalladium complex $C_5H_5PdC_8H_{11}$ (VIII) are discussed, particularly with respect to the stereochemistry of these complexes.

1. Introduction

The reactions of diolefin—metal complexes such as $[DieneMCl_2]$ (Diene = norbornadiene nor-C_7H_8 or 1,5-cyclooctadiene 1,5-C_8H_{12}; M = Pd, Pt) and $[C_5H_5MC_8H_{12}]^+$ (M = Pd, Pt) with anionic nucleophiles, particularly OMe^-, have received considerable attention in recent years [2 - 4]. The stereochemistry of the products obtained, for example, according to eqn. (1) indicated that an *exo*-attack (*trans*-addition) of the methoxide anion on the complexed diene had occurred, whereas in similar reactions of monoolefin palladium compounds, e.g. with OH^-, an *endo*-attack (*cis*-addition) had been postulated [5].

We became interested in these results during our studies on the reactivities

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* For Part XI see ref. 1.

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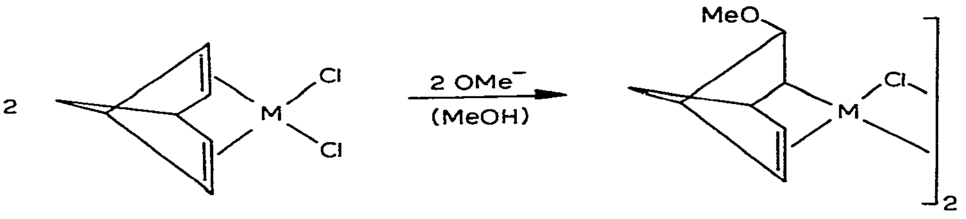
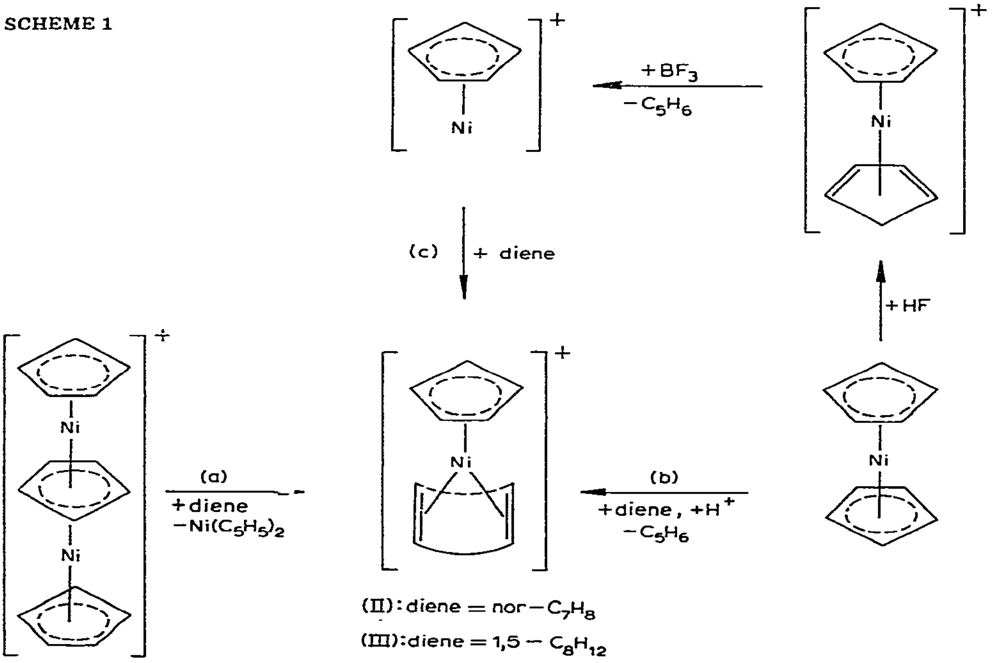


(Ia) $M = Pd$
(Ib) $M = Pt$

of the cationic π-cyclopentadienylnickel diolefin complexes $[C_5H_5Ni(Diene)]^+$ (II: Diene = nor-C_7H_8; III: Diene = 1,5-C_8H_{12}). These can be prepared (as shown in Scheme 1) (a) by the reaction of the three-tier $[Ni_2(C_5H_5)_3]^+$ with the diene in diethyl ether [6,7], (b) by treating a solution of nickelocene and the diene in propionic anhydride with HBF_4 [8], or (c) most directly, by addition of the diene to the coordinatively unsaturated species $[NiC_5H_5]^+$ [9].

SCHEME 1



(II): diene = nor$-C_7H_8$
(III): diene = 1,5 $- C_8H_{12}$

The diene complexes, e.g. (II), react smoothly with neutral Lewis bases L, such as trimethyl phosphite or triphenyl phosphite, to give $[C_5H_5NiL_2]^+$ [8], and, as preliminary experiments have shown, also with a variety of anionic nucleophiles [10]. We now wish to report the reactions of (II) and (III) with the methoxide anion and, in particular, the NMR data of the resultant compounds. It was an additional aim of these studies to resolve some uncertainties arising from conflicting assignments of the NMR spectra of similar complexes.

TABLE 1

NMR DATA OF THE COMPLEXES $C_5H_5MC_7H_8OMe$

In C_6D_6 at 25°; 60 MHz; τ values relative to int. TMS; s = singlet, m = multiplet, dd = doublet of doublets.

Assignment	M = Ni (IV)		M = Pd (V)	
	Chemical shift (τ)	Multiplicity	Chemical shift (τ)	Multiplicity
C_5H_5	4.97	s	4.36	s
OCH_3	6.95	s	6.95	s
H_1	7.50	m	7.25	m
H_{2n}	8.10	m	7.25	m
H_{3x}	6.20	dd	6.17	dd
H_4	7.50	m	7.56	m
$H_{5,6}$	5.34	m	5.15	m
H_{7a}	8.08	m	8.07	m
H_{7s}	8.56	m	8.62	m

2. $C_5H_5NiC_7H_8OMe$ (IV) and $C_5H_5PdC_7H_8OMe$ (V)

Addition of excess sodium methoxide to a solution of (II) in methanol is accompanied by an immediate colour change from orange-brown to deep red. Removal of the solvent followed by extraction of the solid residue with hexane yields an oily product which after subsequent distillation in vacuo analyses as $C_5H_5NiC_7H_8OCH_3$ (IV). The red air-sensitive liquid is easily soluble in most

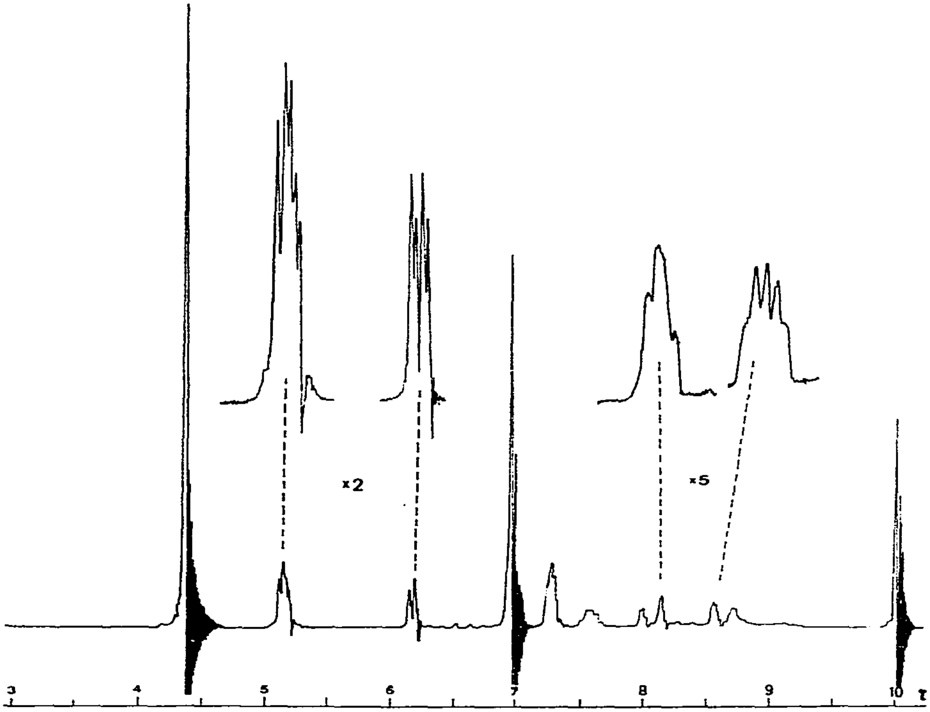
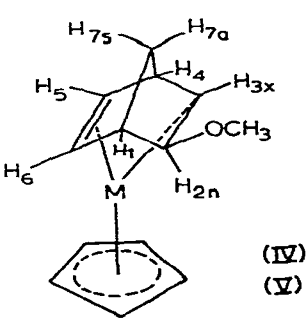


Fig. 1. NMR spectrum of $C_5H_5PdC_7H_8OCH_3$ in C_6D_6.



(IV) M = Ni
(V) M = Pd

organic solvents and thermally stable up to 150°. Infrared bands at 2822 and 1080 cm^{-1} confirm the presence of a OMe group [4].

The NMR spectrum of IV (see Table 1) shows the expected general features for a bicyclo[2.2.1]-hept-2-enyl complex and is in some respects very similar to that described for $[C_7H_8OMePdCl]_2$ (Ia). There are two reports in the literature [2,3] which discuss the NMR data of (Ia). Although both agree that the methoxy substituent must be in the *exo* position with respect to the metal, different assignments for the signals of the H_{2n} and the H_{3x} protons have been suggested. In order to settle that conflict and to enable a correct assignment of the NMR data of (IV) we have synthesised complex (V) by reacting $[C_7H_8OMePdCl]_2$ with TlC_5H_5 in tetrahydrofuran.

The NMR spectrum of (V) in C_6D_6 solution (Fig. 1) consists of eight distinct signals including two sharp singlets due to the h^5-C_5H_5 and OCH_3 protons (see also Table 1). The two non-equivalent olefinic protons, H_5 and H_6, give rise to the multiplet at 5.15 τ while the AB signal at high field corresponds to the bridge hydrogens H_{7a} and H_{7s}. Each line of the low field half of this signal is, itself, a doublet of doublets, showing unequal couplings of 1.1 and 1.6 Hz to the bridgehead protons H_1 and H_4. Each line of the high field half of the signal is, however, a doublet (J 2.0 Hz) of triplets (J 1.1 Hz) indicating, besides coupling to H_1 and H_4, coupling to one other proton. Double irradiation studies confirmed that neither half of the AB type signal is coupled to H_5 or H_6 or to the 6.17 τ signal. The most probable interpretation is that the high field half of the signal corresponds to H_{7s} and that this proton is coupled to the *endo* proton H_{2n}, as such a long range coupling of the order of 2 Hz has previously been observed in various norbornenes [11,12]. The presence of this coupling clearly establishes the stereochemistry at carbon atom C_2, and the *exo* configuration of the methoxy substituent.

The signal at 6.17 τ is assigned to the PdCH proton, H_{3x}, which must be *exo*. Double irradiation of the broad multiplet centred at 7.56 τ showed that the corresponding proton is coupled to both H_{3x} and $H_{5,6}$. The signal can therefore be assigned to the bridgehead proton H_4. The resonances of the remaining protons H_1 and H_{2n} are accidentally coincident forming the multiplet at 7.25 τ. Other measurable coupling constants are $J_{2n,3x}$ 1.0 Hz, $J_{3x,4}$ 2.5 Hz and $J_{7a,7s}$ 9.8 Hz. The NMR data are thus fully consistent with the structure (V) and our assignment is in agreement with that suggested by Green and Hancock [3] for $[C_7H_8OMePdCl]_2$ in that the resonance of the $PdC\underline{H}$ proton H_{3x} appears at considerably lower fields than that of the $C\underline{H}OMe$ proton H_{2n}.

The NMR spectrum of (IV) in C_6D_6 solution is very similar to that of (V) and can be assigned as shown in Table 1. Apart from the expected difference in the chemical shifts of the h^5-C_5H_5 and the olefinic protons $H_{5,6}$ it is noteworthy that the signal of the H_{2n} proton of (IV) is shifted to 8.1 τ compared to 7.25 τ for the corresponding signal of (V). As previously noted, this *endo* proton should experience a pronounced shielding effect due to its proximity to the metal atom [3] and, therefore, the upfield shift in (IV) is entirely consistent with the increased shielding due to the smaller metal atom in the nickel compound.

3. $C_5H_5NiC_8H_{12}OMe$ (VI), $C_5H_5NiC_8H_{11}$ (VII) and $C_5H_5PdC_8H_{11}$ (VIII)

The 1,5-cyclooctadienenickel complex (III) also rapidly reacts with OMe^- in methanol. The NMR spectrum of the red oil obtained after fast distillation of the crude reaction product showed, however, resonances originating from two different compounds present in about a 1/2 ratio. The signals due to the major component included two sharp singlets (intensity ratio 5/3) which indicate the presence of a h^5-C_5H_5 ligand and of a OCH_3 group. It thus seems to be quite obvious that the compound is (VI). The whole NMR spectrum (see Table 2) is rather complex but four separate multiplets each corresponding to one proton can be distinguished. The signals have been assigned by comparison with the NMR data of $C_5H_5PdC_8H_{12}OMe$ [4] and the related nickel complex $C_5H_5NiC_8H_{13}$ [13]. Again it is noticeable that the resonance of the $C\underline{H}OCH_3$ proton of (VI) is shifted upfield by about 0.75 ppm compared with the corresponding signal of the palladium analogue.

The minor component of the oily reaction product from (III) and OMe^- could be obtained in a pure state as red low-melting crystals by slow redistillation of the red oil in vacuo and subsequent chromatography on Al_2O_3. It was characterised by elemental analysis and its mass spectrum as $C_{13}H_{16}Ni$ (VII). The properties of the new compound resemble those of $C_5H_5NiC_3H_5$ [14] and $C_5H_5NiC_5H_7$ [15] indicating the presence of a π-allylic ligand.

The NMR spectrum of (VII) (Table 2) is again complex and we are unable to give a full interpretation. However, in addition to the sharp resonance of the h^5-C_5H_5 protons the spectrum shows two broad signals at low field assigned to two uncoordinated olefinic protons, H_5 and H_6, three other distinct multiplets

TAB[illegible]

N[illegible]A OF $C_5H_5NiC_8H_{12}OMe$ (VI) AND $C_5H_5NiC_8H_{11}$ (VII)

[illegible] D_6 at 25°; 60 MHz; τ values relative to int. TMS; s = singlet, t = triplet, m = multiplet.

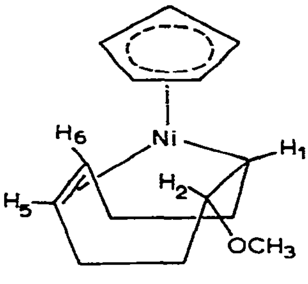
Assignment (VI)	Chemical shift (τ)	Multiplicity	Assignment (VII)	Chemical shift (τ)	Multiplicity
C_5H_5	5.08	s	C_5H_5	4.96	s
OCH_3	6.87	s			
H_1	7.22	m	H_1, H_3	7.20 7.7^a	m
H_2	6.70	m	H_2	5.95	t^b
H_5, H_6	5.38 6.30	m	H_5, H_6	4.47 4.8^a	m
4 X CH_2	7.6 - 8.6	m	3 X CH_2	7.8 - 8.2	m

^{a}Approximate values only. ^{b}J 7.5 Hz.

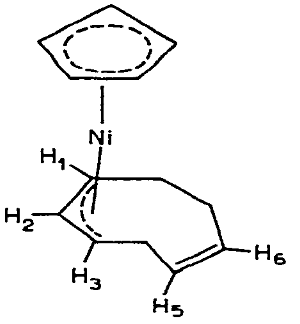
each corresponding to one proton (H_1, H_2 and H_3), and the very wide signal due to the methylene protons. The spectrum is thus consistent with structure (VII) and we suggest that the complex is formed by loss of methanol from VI according to eqn. (2). The position of the free double bond in (VII) could not be exactly determined from the NMR data but it seems unlikely that under the conditions used for the formation of (VII) a rearrangement of this double bond would occur.

$$\underset{\text{(III)}}{[C_5H_5NiC_8H_{12}]^+} \xrightarrow{+\,OMe^-} \underset{\text{(VI)}}{C_5H_5NiC_8H_{12}OMe} \xrightarrow{-MeOH} \underset{\text{(VII)}}{C_5H_5NiC_8H_{11}} \qquad (2)$$

Metal complexes containing the cyclooctadienyl ligand C_8H_{11} have been recently reported by various research groups. Lewis et al. have prepared the cations $[C_5H_5MC_8H_{11}]^+$ (M = Co, Rh, Ir) both by hydride abstraction from $C_5H_5M(1,5\text{-}C_8H_{12})$ [16] and also by protonation of $C_5H_5M(1,3,5\text{-}C_8H_{10})$ [17]. The C_8H_{11} ligand in these cations may be coordinated as a *trihapto* (1,3,4-η-bonded) or as a *pentahapto* (1,2,3,4,5-η-bonded or 1,2,3,5,6-η-bonded) system, the *pentahapto* types allowing the metal to obtain an inert gas configuration. The NMR spectra of $[C_5H_5Co(1,2,3,5,6\text{-}\eta\text{-}C_8H_{11})]^+$ and (VII) have certain similarities which support the structural proposal for the nickel complex.



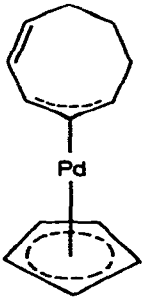
(VI)



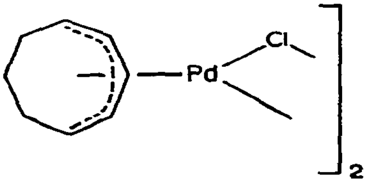
(VII)

The binuclear cyclooctadienylpalladium complex $[C_8H_{11}PdCl]_2$ has been prepared by Robinson and Shaw [4] from 1,3-cyclooctadiene and sodium tetrachloropalladite in boiling methanol and by Hüttel et al. [18] from 1,3-cyclooctadiene and palladium dichloride in 50% aqueous acetic acid. The first method involves the intermediate formation of a methoxide substituted cyclooctenyl complex [similar to (VI)] which then, again by loss of methanol, reacts to give the cyclooctadienyl complex $[C_8H_{11}PdCl]_2$.

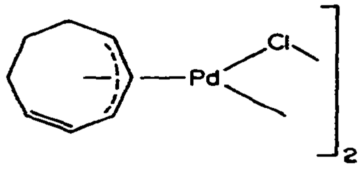
Both Shaw [4] and Hüttel [18] discussed the structure of $[C_8H_{11}PdCl]_2$ in terms of two different coordination modes. However, while Shaw favoured the symmetrically bonded structure (IX) in which all the five sp^2 hybridised carbon atoms are linked to the metal atom, Hüttel used the complexity of the NMR spectrum of the compound to suggest an α,β-unsaturated π-allylic structure (X) analogous to that found in (VII).



(VIII)



(IX)



(X)

Using the methods of Robinson and Shaw [4], we have prepared $[C_8H_{11}PdCl]_2$ and $C_5H_5PdC_8H_{11}$ (VIII). Our NMR measurements clearly support the proposed structure (X) for the binuclear complex. Although as previously noted [18], the NMR spectrum is very complex, it does show at least four and probably five distinct resonances at low field. Double irradiation at various frequencies of the methylene resonance helped to confirm this. The more symmetrical structure (IX) should give rise to a maximum of only three separate resonances at low field. Indeed the NMR spectra of one type of isomer of $[C_5H_5MC_8H_{11}]^+$ (M = Co, Rh, Ir) [17], suggested to have a structure related to (IX), show apart from signals due to the h^5-C_5H_5 and methylene protons only two complex resonances in a 1/4 intensity ratio.

The NMR spectrum of (VIII) demonstrates that the protons attached to unsaturated carbon atoms in this complex have very similar chemical shifts to the corresponding protons in $[C_8H_{11}PdCl]_2$. It seems very unlikely that the h^5-cyclopentadienyl complex would have a structure related to (IX) as this would lead to a 20 electron configuration at the metal. The large difference in chemical shifts between the allylic protons of (VII) and (VIII) is further evidence for the proposed difference in the double bond position in these compounds.

There is no obvious reason why the 2-methoxy-5-cyclooctenyl-1-palladium chloro complex prepared from sodium chloropalladite and 1,5-cyclooctadiene [4], is unchanged upon heating in methanol for two hours whereas the reaction of (VI) to give (VII) is facile.

Experimental

All experiments were carried out under nitrogen, using solvents that were purified under nitrogen by standard procedures. NMR measurements were made on JEOL-C-60-HL and IR spectra were obtained on a Beckman IR-12.

(a). $C_5H_5NiC_7H_8OCH_3$

500 mg (9.75 mmole) $NaOCH_3$ was added to 1.5 g (4.95 mmole) $[C_5H_5NiC_7H_8]BF_4$ [8] dissolved in methanol to give, immediately, a red solution. After stirring for a few minutes the solvent was removed under reduced pressure and the solid residue extracted with hexane. After filtering the hexane solution over a G3 fritted disk covered with cotton wool, the filtrate was transferred to a 100 ml flask and the hexane distilled off in vacuo. At 50 — 70° and 10^{-3} mm a small amount of nickelocene could be caught on a cooled finger and removed from the system. At somewhat higher temperatures (80 - 100°), a red liquid distilled into a small Schlenk tube. Yield 625 mg, 51%. (Found: C, 63.44; H, 6.52; Ni, 23.53. $C_{13}H_{16}NiO$ calcd.: C, 63.22; H, 6.52; Ni, 23.77%.)

IR (cm^{-1}) in KBr: 700 w, 800 s, 845 m, 880 m, 890 m, 910 m, 920 m, 960 w, 980 w, 1000 m, 1020 m, 1030 m, 1045 m, 1080 s, 1110 m, 1140 m, 1170 m, 1195 m, 1220 w, 1230 w, 1250 w, 1285 m, 1305 m, 1350 m, 1375 m, 1420 w, 1450 m, 1460 m, 2380 w, 2822 m, 2900 s, 2940 s, 2990 s, 3100 w.

(b). $C_5H_5PdC_7H_8OCH_3$

1 g (1.885 mmole) $[C_7H_8OCH_3PdCl]_2$, prepared according to ref. 3, was treated with 1.06 g (3.94 mmole) TlC_5H_5 in 50 ml tetrahydrofuran. After stirring the solution at room temperature for 30 min, the solvent was removed in vacuo and the solid residue extracted with 30 ml pentane. Filtration of the pentane solution over a G3 fritted disk covered with cotton wool and removal of the solvent gave a dark red oil. Yield 800 mg, 72%. (Found: C, 53.19; H, 5.55. $C_{13}H_{16}OPd$ calcd.: C, 52.98; H, 5.47%.)

(c). $C_5H_5NiC_8H_{11}$

Reaction of $[C_5H_5NiC_8H_{12}]BF_4$ [8] with $NaOCH_3$ in methanol and isolation of the crude reaction product as in (a). During subsequent distillation at 10^{-3} mm the temperature was slowly raised to 60 - 70° allowing the sublimation of small amounts of nickelocene. Further distillation at 110° produced a red oil which solidified on cooling. This product was dissolved in hexane and the solution chromatographed over an Alox column (activity grade IV). The major red-brown fraction was collected and the solvent removed in vacuo. Yield of red-brown crystals (m.p. 39°) 35%. (Found: C, 67.74; H, 6.74; Ni, 25.20. $C_{13}H_{16}Ni$ calcd.: C, 67.60; H, 6.98; Ni, 25.41%.)

IR (cm^{-1}) in KBr: 470 w, 600 w, 660 w, 670 w, 705 m, 790 s, 845 m, 870 w, 885 w, 940 w, 945 w, 995 m, 1015 m, 1040 m, 1055 m, 1115 w, 1160 w, 1190 w, 1210 w, 1240 m, 1305 m, 1350 w, 1390 w, 1420 w, 1440 w, 1650 w, 2380 m, 2830 w, 2940 m, 3000 w.

Mass spectrum (relative intensities), *m/e*: 230 (50) M^+, 202 (10) $(M - C_2H_4)^+$, 188 (4) $NiC_{10}H_{10}^+$, 164 (72) $NiC_8H_{10}^+$, 136 (100) $NiC_6H_6^+$, 124 (17) $NiC_5H_6^+$, 123 (19) $NiC_5H_5^+$.

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References

1 G. Parker and H. Werner, Helv. Chim. Acta, in press.
2 J.K. Stille and R.A. Morgan, J. Amer. Chem. Soc., 88 (1966) 5135.
3 M. Green and R.I. Hancock, J. Chem. Soc., A, (1967) 2054.
4 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1964) 5002; B.L. Shaw, Chem. Commun., (1968) 464.
5 P.M. Henry, J. Amer. Chem. Soc., 86 (1964) 3246.
6 A. Salzer and H. Werner, Syn. Inorg. Metal-org. Chem., 2 (1972) 249.
7 A. Salzer and H. Werner, Angew. Chem., 84 (1972) 949; Angew. Chem., Int. Ed. Engl., 11 (1972) 930.
8 A. Salzer, T.L. Court and H. Werner, J. Organometal. Chem., 54 (1973) 325.
9 T.L. Court and H. Werner, J. Organometal. Chem., 54 (1973) 325.
10 A. Salzer, unpublished results.
11 P. Laszlo and P. von R. Schleyer, J. Amer. Chem. Soc., 86 (1964) 1171.
12 J.C. Davis Jr. and T.V. van Auken, J. Amer. Chem. Soc., 87 (1965) 3900.
13 K.W. Barnett, J. Organometal. Chem., 21 (1970) 477.
14 E.O. Fischer and G. Bürger, Chem. Ber., 94 (1961) 2409; W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc., 83 (1961) 1601.
15 E.O. Fischer and H. Werner, Chem. Ber., 92 (1959) 1423; 95 (1962) 695.
16 J. Lewis and A.W. Parkins, J. Chem. Soc. A, (1967) 1150; (1969) 422.
17 J. Evans, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1972) 2668.
18 R. Hüttel, H. Dietl and H. Christ, Chem. Ber., 97 (1964) 2037.