Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTION OF BIS(1,5-CYCLOOCTADIENE)NICKEL WITH CYCLOPENTADIENE AND METHYLCYCLOPENTADIENE: FORMATION OF NOVEL σ,π-CYCLOOCTENYL COMPLEXES

KENNETH W. BARNETT
Shell Development Company, Emeryville, California (U.S.A.)

(Received October 10th, 1969)

SUMMARY

Bis(1,5-cyclooctadiene)nickel reacts smoothly with cyclopentadiene or methylcyclopentadiene to afford the new complexes π-$C_5H_5NiC_8H_{13}$ (I), and π-$CH_3C_5H_4$-NiC_8H_{13} (II), respectively. NMR spectra suggest that the C_8H_{13} fragments are bonded to nickel via one sigma and one pi-olefinic bond. The mechanism of formation of these complexes is believed to involve a mixed cyclopentadiene-cyclooctadiene nickel complex which undergoes a metal-assisted hydride shift from the five-membered ring to cyclooctadiene. Both (I) and (II) are apparently inert to substitution by tertiary phosphines or phosphites, but (I) undergoes carbon monoxide insertion to form the unstable π-$C_5H_5NiCOC_8H_{13}$, characterized by mass spectrometry.

INTRODUCTION

The reaction of cyclopentadiene with low-valent metal complexes to generate π-C_5H_n metal compounds ($n=5$, 6, or 7) is a general phenomenon. The nature of the product isolated in any given instance is dependent upon reaction conditions, the metal, and the attached ligands. These factors are illustrated by the diverse complexes isolated from the reactions of cyclopentadiene with $Ni(CO)_4$[1], $Co_2(CO)_8$[2], $Fe(CO)_5$[2], $Fe_2(CO)_9$[3], $Mo(CO)_6$[4], $(CH_3CN)_3W(CO)_3$[5], and $[(C_6H_{11})_3P]_2Ni$[6]. Cyclopentadienylmetal hydrides are believed[3,5,7] to be intermediates in the reactions involving metals bearing only carbon monoxide ligands, but such species are not stable under the forcing conditions required to replace the carbonyl groups[2,4,7]. Hydrido complexes are isolated from the reactions with $(CH_3CN)_3W(CO)_3$[5] and $[(C_6H_{11})_3P]_2Ni$[6], however, due in part to the facile replacement of the nitrile ligands in the tungsten complex and the coordinatively unsaturated nature of $[(C_6H_{11})_3P]_2Ni$.

To our knowledge similar reactions of metal complexes containing olefin ligands have not been studied. We have therefore investigated the course of the reactions of cyclopentadiene and methylcyclopentadiene with $(COD)_2Ni$ (COD = 1,5-cyclooctadiene)[8a].

EXPERIMENTAL

All operations were conducted under nitrogen or argon atmospheres. Bis(1,5-cyclooctadiene)nickel was prepared by the method of Wilke, *et al.*[8a] from anhydrous nickel(II) acetylacetonate (Alpha Inorganics), COD, and triethylaluminum (Texas Alkyls). Solvents were stored over Linde Molecular Sieves and flushed with dry nitrogen prior to use. Cyclopentadiene and methylcyclopentadiene (Columbia) were obtained by thermal cracking of the corresponding dimers and used immediately. Proton NMR spectra were taken in deuterobenzene (Diaprep, Inc.) solution (internal tetramethylsilane standard) on a Varian Associates A-60 spectrometer. Double irradiation measurements were accomplished on a modified Varian HA-100 instrument. Mass spectral data were recorded on a CEC Model 21-110B High Resolution Mass Spectroscope (70 eV) with C_8-C_{10} fluorocarbons and xenon as internal mass markers. Samples were introduced directly into the inlet probe at approximately 100° and data recorded on photographic plates. These data were reduced using computer techniques described by Tunnicliff and Wadsworth[9]. GLC analyses were performed on a Varian-Aerograph Model 1520 instrument with a 20 foot SE-30 on Chromosorb-W column, utilizing a hydrogen flame detector.

Reaction of cyclopentadiene with $(COD)_2Ni$

The nickel complex (7.1 g, 26 mmoles) and approximately 50 ml of dry benzene were charged under argon to a 200 ml three-necked flask equipped with reflux condenser, magnetic stirrer, and pressure-compensating dropping funnel. To this slurry was added dropwise a solution of 11 ml of freshly-cracked cyclopentadiene (130 mmoles) in an additional 20 ml of benzene. The addition was carried out at room temperature with vigorous stirring. The previously undissolved $(COD)_2Ni$ quickly went into solution and the color of the reaction mixture changed from yellow to deep red in approximately 15 min. The solution was stirred at 25° for 17 h to insure complete reaction. The red solution was filtered under argon and the solvent removed at aspirator vacuum. The residue was distilled at 0.1 mm and 75–82°, two fractions being collected. The first (approximately 0.8 g, 75–80°) contained a substantial amount of cyclopentadiene plus traces of the known π-C_5H_5Ni-C_5H_7[1]. The second cut [80–82°, 3.7 g, 65% yield based on $(COD)_2Ni$] was analytically pure. (Found: C, 67.4; H, 7.9; Ni, 24.7; mol.wt. mass spec., 232. $C_{13}H_{18}Ni$ calcd.: C, 66.95; H, 7.72; Ni, 25.3%; mol.wt., 232.) Hydrogenation of a portion of the product with palladium on charcoal catalyst afforded a 1/1 ratio of cyclopentane and cyclooctane, identified by GLC. The red liquid product is decomposed by air but appears to be stable indefinitely at room temperature when protected from the atmosphere.

Reaction of methylcyclopentadiene with $(COD)_2Ni$

This preparation was carried out in identical fashion to that described above for cyclopentadiene. Distillation at 0.1 mm and 60–65° afforded 4.6 g of red liquid π-$CH_3C_5H_4NiC_8H_{13}$, 71% yield. As above, an earlier one gram fraction was discarded due to entrained diene and a small amount of π-$CH_3C_5H_4Ni\pi$-$CH_3C_5H_6$[10] as shown by mass spectroscopy. The second cut (63–65°) analyzed correctly for $C_{14}H_{20}$-Ni. (Found: C, 69.2; H, 8.1; Ni, 22.7; mol.wt. (mass spec.), 246. $C_{14}H_{20}Ni$ calcd.: C, 68.02; H, 8.10; Ni, 23.98%; mol.wt., 246) Hydrogenation of this complex affords methylcyclopentane and cyclooctane as the only hydrocarbon products. The air sensitivity of the complex parallels that of the cyclopentadiene analog. Subsequent experience has shown that the amount of cyclopentadiene or methylcyclopentadiene may be cut by as much as 50% without a sacrifice in yield or facility of these reactions. This simplifies the distillation.

Attempts to extend these reactions to include indene and 1,3-cyclohexadiene led only to decomposition and the desired π-indenyl and π-cyclohexadienyl complexes could not be isolated.

Attempted reactions of π-$C_5H_5NiC_8H_{13}$ and π-$CH_3C_5H_4NiC_8H_{13}$ with phosphorus ligands

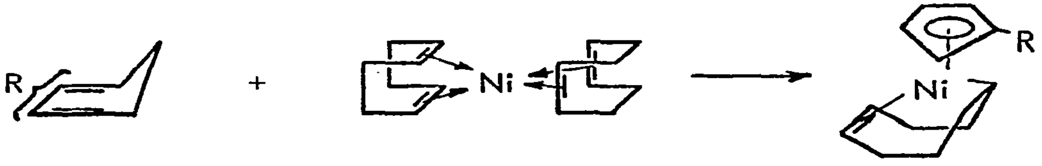
Equimolar amounts of the organonickel complexes and triphenylphosphine, trimethylphosphite, or tributylphosphine could be refluxed in benzene or toluene solution for up to 20 h without formation of substitution products. This lack of reaction was confirmed by proton NMR and mass spectral analysis of the recovered starting materials. UV irradiation of benzene solutions of (I) or (II) with tributylphosphine were likewise unsuccessful in bringing about substitution.

Reaction of π-$C_5H_5NiC_8H_{13}$ with carbon monoxide

Twenty ml of cyclohexane and 0.5 g (I) (2.15 mmoles) were charged under nitrogen to an 84 ml stainless steel autoclave equipped with magnetic stirrer. The vessel was pressured to 400 psi with CO (Matheson, 99%) and stirred at 50° for 18 h. The IR spectrum of the degassed product mixture showed the presence of $Ni(CO)_4$ and additional strong bands at 1705 and 1665 cm^{-1}. GLC analysis showed two products emerging before the cyclohexane solvent and at least ten other peaks. Similar analysis of (I) in cyclohexane shows only C_5 and C_8 products (two peaks in addition to cyclohexane). Chromatography on a neutral Woehlm alumina column (15 × 1.5 cm) afforded traces of (I) as the only nickel containing species. The mass spectrum of the crude reaction mixture exhibited a parent ion corresponding to $C_5H_5NiCOC_8H_{13}^+$, verified by the expected nickel isotope pattern. Additional ions assigned to $(C_5H_5)_2Ni_2^+$, $(C_5H_5)_2Ni^+$, $C_8H_{13}COC_8H_{13}^+$, $C_8H_{13}COC_5H_5^+$ and (I) were also observed. Repeated attempts to isolate $C_5H_5NiCOC_8H_{13}$ were unsuccessful. More forcing conditions caused greater conversions to $Ni(CO)_4$ and milder conditions (*e.g.* 80°, 1 atm) were insufficient for the insertion reaction to occur.

DISCUSSION

In 1952, Miller, Tebboth, and Tremaine reported the reaction of cyclopentadiene with elemental iron at elevated temperatures to form ferrocene[11]. Metal carbonyls or their derivatives have since proven to be fruitful substrates for this type of direct thermal reaction, yielding complexes containing cyclopentadienyl[1-4], cyclopentadiene[3], or cyclopentenyl[1] ligands π-bonded to the metal atom. We have found that $(COD)_2Ni$ (COD = 1,5-cyclooctadiene) reacts smoothly with cyclopentadiene or methylcyclopentadiene at room temperature to form complexes in which one of the COD ligands is displaced. The remaining C_8 fragment has undergone addition of a hydrogen atom and is apparently attached to nickel via one sigma and one pi olefin bond. This type of bonding has recently been demonstrated by an X-ray



(I), R = H
(II), R = CH_3

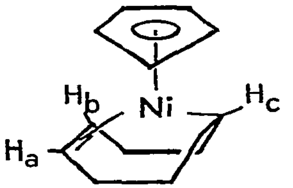
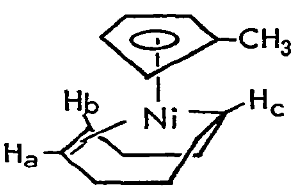
diffraction study of $(Acac)NiC_8H_{13}$[8b] (Acac = acetylacetonato). The C_5H_5 (I) and $CH_3C_5H_4$ (II) ligands are bonded in normal π-cyclopentadienyl fashion.

Both complexes are viscous red liquids, soluble in common organic solvents, and air sensitive both neat and in solution. Exhaustive catalytic hydrogenation affords saturated hydrocarbons expected for the assigned formulations. (See experimental.)

The proton NMR spectrum of π-$C_5H_5NiC_8H_{13}$ (deuterobenzene) consists of a sharp singlet at $\delta = 5.03$ ppm and broad multiplets at $\delta = 4.70$, 3.85, 2.69, and 1.2 ppm of relative intensities 5/1/1/1/10 (Table 1). The resonance at 5.03 ppm is readily

TABLE 1

PROTON NMR DATA FOR π-$C_5H_5NiC_8H_{13}$ AND π-$CH_3C_5H_4NiC_8H_{13}$[a]

Compound	δ (ppm)	Rel. intensity	Multiplicity[b]	Assignment
	5.03	5	S	C_5H_5
	4.70	1	M[c]	H_a (or H_b)
	3.85	1	M[c]	H_b (or H_a)
	2.69	1	M[c]	H_c
	1.2[d]	10	M	Methylene
	4.97	4	Double triplet	C_5H_4
	4.60	1	M[c]	H_a (or H_b)
	3.76	1	M[c]	H_b (or H_a)
	2.47	1	M[c]	H_c
	1.70	3	S	CH_3
	1.3[d]	10	M	Methylene

[a] Deuterobenzene, TMS internal standard, 60 MHz. [b] S = singlet, M = multiplet. [c] These resonances are 15–20 Hz wide, due apparently to complex spin–spin interactions. The C_5H_5 and CH_3 resonances are extremely sharp in the same samples. [d] These positions are the geometric center of multiplets which are ~120 Hz wide.

assigned to the five equivalent cyclopentadienyl protons. The very broad (~120 Hz) featureless resonance centered at $\delta = 1.2$ ppm is assigned to the ten methylene protons of the cyclooctenyl ligand. The 1/1/1 pattern is due to the two olefinic protons H_a

and H_b (4.70 and 3.85 ppm) and the unique proton H_c ($\delta = 2.69$ ppm, Table 1). Decoupling of the 4.70 and 3.85 ppm resonances (in the 100 MHz spectrum) has no effect on the resonance at δ 2.69, demonstrating that these protons (H_a,H_b) are not coupled to H_c. Irradiation of the low field portion of the methylene region collapses the H_a and H_b resonances to doublets ($J_{ab} = 3.5$ Hz). These observations allow rigorous assignment of the 4.70 and 3.85 ppm resonances to the *cis*-vinylic protons H_a and H_b. The relatively large differences in chemical shifts for H_a and H_b may be due to their having different proximities to the nickel atom[12]. Inspection of molecular models suggests that this non-equivalence is the result of constraints placed on the C_8 ring by the presence of the nickel–carbon sigma bond. The proton spectrum of (Acac)NiC_8H_{13} also exhibits this feature[8a].

The complex π-$CH_3C_5H_4NiC_8H_{13}$ gives rise to a qualitatively similar NMR spectrum, perturbed by the presence of the methyl group on the cyclopentadienyl ring. Thus the cyclopentadienyl protons are no longer equivalent and this resonance ($\delta = 4.97$ ppm) approximates the double triplet expected for monosubstituted cyclopentadienylmetal complexes[13]. The methyl absorption appears as a sharp singlet (1.70 ppm) superimposed on the cyclooctenyl methylene resonance. The 1/1/1 pattern for H_a, H_b and H_c is once again a feature of the spectrum (Table 1).

The mass spectra of (I) and (II) provide further evidence in support of the assigned structures (Table 2). Parent ions are observed for both complexes as are intense $C_8H_{12}Ni^+$ fragments. The latter observation indicates that a major fragmentation pathway for these complexes involves the formal loss of cyclopentadiene [or methylcyclopentadiene for (II)] from the parent ion; similar behavior has recently been reported for β-diketone cyclooctenyl complexes of palladium and platinum[14]. The ion $C_4H_6Ni^+$ also occurs in high relative abundance for both (I) and (II). King[15] has observed the ion π-$C_5H_5RhC_4H_6^+$ in the spectrum of the structurally similar π-$C_5H_5RhC_8H_{12}$ and suggested that butadiene is extruded from the coordinated

TABLE 2

NICKEL-CONTAINING IONS IN THE MASS SPECTRA OF π-$C_5H_5NiC_8H_{13}$ AND π-$CH_3C_5H_4NiC_8H_{13}$ (70 eV)[a]

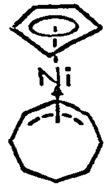
π-$C_5H_5NiC_8H_{13}$			π-$CH_3C_5H_4NiC_8H_{13}$		
m/e	Ion[b]	Relative intensity	*m/e*	Ion[b]	Relative intensity
232	$C_{13}H_{18}Ni^+$ [c]	31	246	$C_{14}H_{20}Ni^+$ [c]	15
166	$C_8H_{12}Ni^+$	100	166	$C_8H_{12}Ni^+$	100
124	$C_5H_6Ni^+$	5	124	$C_5H_6Ni^+$ [d]	5
123	$C_5H_5Ni^+$	18	123	$C_5H_5Ni^+$ [d]	9
112	$C_4H_6Ni^+$	54	112	$C_4H_6Ni^+$	257
97	$C_3H_3Ni^+$	6	97	$C_3H_3Ni^+$	3
84	$C_2H_2Ni^+$	2	84	$C_2H_2Ni^+$	4
58	Ni^+	69	58	Ni^+	218

[a] CEC Model 21-110B High Resolution Mass Spectroscope, xenon and C_8–C_{10} fluorocarbons as internal mass markers. Data reduced using computer techniques described by Tunnicliff and Wadsworth[9]. [b] Ions shown contain ^{58}Ni; ^{60}Ni; and ^{62}Ni ions observed in approximate natural abundance but are eliminated for clarity. [c] Parent ion. [d] See text for a discussion of the absence of π-$CH_3C_5H_4Ni^+$ and π-$CH_3C_5H_5Ni^+$ ions.

cyclooctadiene ligand. This may well be the case for the $C_8H_{12}Ni^+$ ion but the complexity of the spectra and the limitations of our current data reduction system prohibit a cracking-pattern analysis at present. It is interesting to note that $C_8H_{12}Pt^+$ apparently does not fragment to $C_4H_6Pt^+$ [14], nor does π-$C_5H_5CoC_8H_{12}$[16] exhibit a detectable $[P-C_4H_6]^+$ ion[17] analogous to that observed for the corresponding rhodium complex.

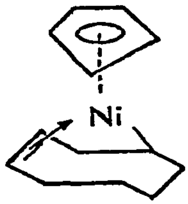
The spectrum of (I) also shows $C_5H_6Ni^+$, $C_5H_5Ni^+$ and $C_3H_3Ni^+$ fragments usually associated with π-C_5H_5M complexes[18]. These ions are present in the case of (II), but the methyl-substituted analogs $CH_3C_5H_5Ni^+$, $CH_3C_5H_4Ni^+$ and CH_3-$C_3H_2Ni^+$ are not observed. The latter observation is qualitatively consistent with the low relative abundances observed for $RC_5H_4Fe^+$ fragments in the spectra of monosubstituted ferrocenes[19,20]. The intensities of the $C_8H_{12}Ni^+$, $C_4H_6Ni^+$, and Ni^+ ions (relative to P^+) also indicate that methylcyclopentadiene is lost more readily than is cyclopentadiene (Table 2). It is not known whether these processes occur prior or subsequent to ionization. The possibility exists that the $C_5H_nNi^+$ ($n=5$ or 6) species for both (I) and (II) are fragments of $C_8H_{12}Ni^+$. These questions may possibly be answered by a detailed cracking pattern analysis, which will be undertaken shortly*.

An alternative method of bonding the C_8H_{13} fragment to nickel is via a π-allyl interaction. If this were the case, however, the NMR spectrum of (I) would be expected to exhibit a 1/2/10 cyclooctenyl pattern analogous to those observed for $C_8H_{12}Co$-π-C_8H_{13}[21] and $[(C_6H_5)_3P]_2Rh$-π-C_8H_{13}[22]. Furthermore, the low field, relative intensity one resonance should occur as a well resolved triplet[21,22] and this also is inconsistent with our data. Taken together with the mass spectral data, these observations serve to eliminate π-allylic C_8H_{13} formulations for both (I) and (II).



(I)

We are unable to exclude the possibility that the cyclooctenyl groups in these complexes are bonded to nickel in a 1,4 fashion, *i.e.*,

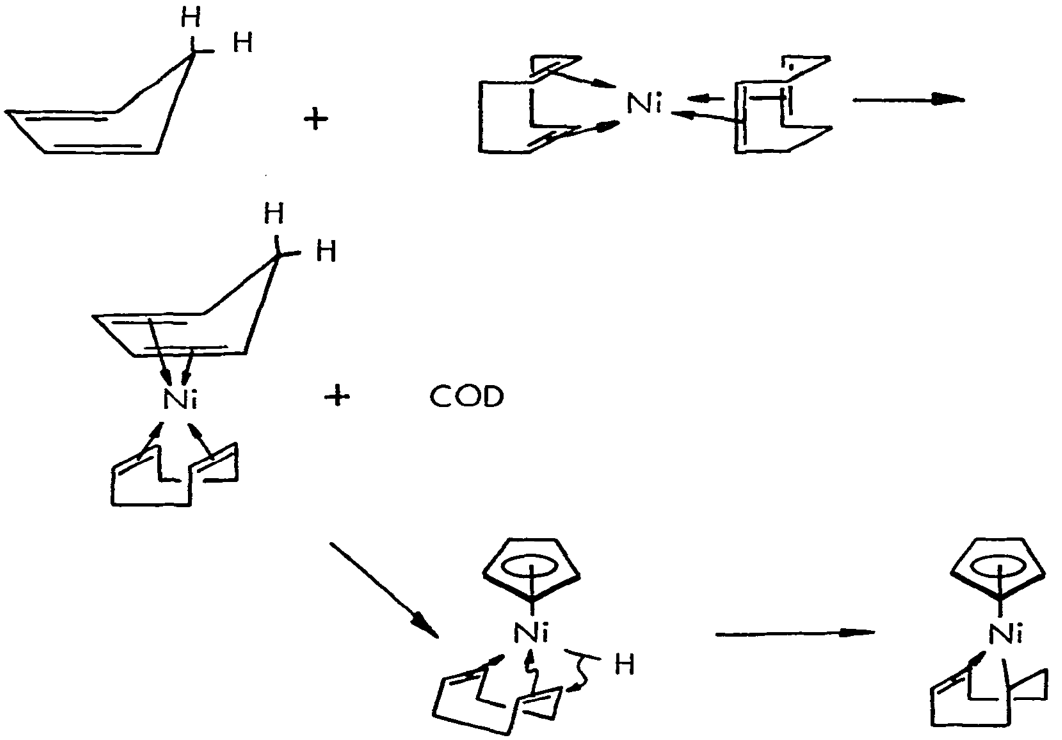


---

[*] *Note added in proof*: King[26] has recently presented mass spectral data for some nickel, palladium, and platinum cyclopentadienyl complexes exhibiting preferential loss of C_5H_6 from the respective parent ions. In the same paper a detailed cracking pattern analysis of π-$C_5H_5M(C_8H_{12})$ complexes ($M = Rh, Ir$) is given.

This seems less likely than the suggested 1,5 attachment, however, in view of the unfavorable steric requirements of such an arrangment and the precedence for 1,5 bonding in similar complexes of nickel[8], palladium[14], and platinum[14].

A likely mechanism for the formation of (I) and (II) involves formation of a mixed cyclopentadiene-cyclooctadiene complex (Fig. 1). Migration of a hydrogen atom from cyclopentadiene to nickel generates a cyclopentadienylnickel hydride species, followed by insertion of one of the COD olefinic linkages into the nickel–hydrogen bond to form the product. Although a distinct metal hydride intermediate is shown this need not be the true state of affairs; the important feature of the proposed mechanism is the intimate involvement of the nickel atom in the hydrogen transfer step. The nickel atom may merely provide a low energy pathway for the migration without a genuine nickel–hydrogen bond being generated.



(I)

Fig. 1. Proposed mechanism for the reaction cyclopentadiene with $(COD)_2Ni$.

Analogous mechanisms have been proposed for the reactions of $Fe(CO)_5$[7], $Mo(CO)_6$[7], and $(CH_3CN)_3W(CO)_3$[5] with cyclopentadiene. Only in the case of $(CH_3CN)_3W(CO)_3$ is an intermediate hydrido species isolated. This may be in part attributable to the great thermal and oxidative stability of π-$C_5H_5W(CO)_3H$ relative to corresponding complexes of iron, molybdenum and nickel[23]. However, the reactions of $Fe(CO)_5$ and $Mo(CO)_6$ are conducted at elevated temperatures, under which conditions the incipient hydrides are readily decomposed into dimeric products and hydrogen. This has been elegantly demonstrated by Kochhar and Pettit who showed that $C_5H_6Fe(CO)_3$ is indeed decomposed to $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ at 140° in the presence of hydrogen acceptors[3]. Further evidence along these lines is provided by the observation that cyclopentadiene and $[(C_6H_{11})_3P]_2Ni$ react to afford $\pi\text{-}C_5H_5Ni(H)[P(C_6H_{11})_3]$[6]. The "trapping" of this nickel hydride is no doubt due in large measure to the stabilizing effect of the tricyclohexylphosphine ligand[6].

The product of the reaction between cyclopentadiene and $Ni(CO)_4$ was originally reported as $(C_5H_6)_2Ni$[1], but NMR studies[24] led to reassignment as $\pi\text{-}C_5H_5Ni\text{-}\pi\text{-}C_5H_7$. Methylcyclopentadiene and nickel carbonyl similarly afford $\pi\text{-}CH_3C_5H_4Ni\text{-}\pi\text{-}CH_3C_5H_6$[10]. These complexes are probably formed by mechanisms analogous to those proposed for (I) and (II). This is consistent with our observation of these complexes in trace amounts in the corresponding reactions with $(COD)_2Ni$. It appears that $(C_5H_6)_2Ni$, as yet not isolable, may well be an unstable intermediate in the formation of the actual product.

The reaction of $\pi\text{-}C_5H_5NiC_8H_{13}$ with carbon monoxide is exceedingly complex. No nickel-containing species could be isolated by conventional means but a combination of IR and mass spectral evidence shows the products to be $\pi\text{-}C_5H_5NiCOC_8H_{13}$, $Ni(CO)_4$, $(\pi\text{-}C_5H_5)_2Ni$, and possibly $[\pi\text{-}C_5H_5Ni(CO)]_2$. In addition, a variety of organic ketones, etc. are produced (see experimental). These observations are consistent with insertion of carbon monoxide into the nickel–carbon sigma bond of (I) to afford the unstable $\pi\text{-}C_5H_5NiCOC_8H_{13}$. (The apparent instability of cyclopentadienylnickel acyls has been commented on previously[25].) Decomposition and/or further reaction with CO could reasonably lead to the observed spectrum of products. Moderate pressures (150–400 psi) are required for these conversions, and this relative inertness is consistent with the lack of reactivity shown by both (I) and (II) toward tertiary phosphines and phosphites. Molecular models of these complexes show the nickel atom to be highly shielded by the organic ligands, suggesting that the low reactivity of (I) and (II) towards substitution is probably of steric origin.

ACKNOWLEDGEMENTS

The author is indebted to Mr. G. W. Schoenthal for expert technical assistance, Mr. P. A. Wadsworth for obtaining the mass spectral data, and to Dr. W. Keim and Dr. F. D. Mango for valuable discussions.

REFERENCES

1 E. O. FISCHER AND H. WERNER, *Chem. Ber.*, 92 (1959) 1423.
2 T. S. PIPER, F. A. COTTON AND G. WILKINSON, *J. Inorg. Nucl. Chem.*, 1 (1955) 165.
3 R. K. KOCHHAR AND R. PETTIT, *J. Organometal Chem.*, 6 (1966) 272.
4 G. WILKINSON, *J. Amer. Chem. Soc.*, 76 (1954) 209.
R. G. HAYTER, *Inorg. Chem.*, 2 (1963) 1031.
5 R. B. KING AND A. FRONZAGLIA, *Inorg. Chem.*, 5 (1966) 1837.
6 K. JONAS AND G. WILKE, *Angew. Chem.*, 81 (1969) 534.
7 H. W. STERNBERG AND I. WENDER, *Papers Presented at the International Conference on Coordination Chemistry, London, April, 1959, Chemical Society Special Publication No. 13*, The Chemical Society, London, 1960, p. 41.
8 (a) B. BOGDANOVIC, M. KRONER AND G. WILKE, *Ann. Chem.*, 699 (1966) 1;
(b) O. S. MILLS AND E. PAULUS, *Chem. Commun.*, (1966) 738.
9 D. D. TUNNICLIFF AND P. A. WADSWORTH, *Anal. Chem.*, 40 (1968) 1826.

10 E. O. Fischer and H. Werner, *Chem. Ber.*, 95 (1962) 695.
11 S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, (1952) 632.
12 A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, (1964) 2747.
13 J. Lewis and A. W. Parkins, *J. Chem. Soc., A*, (1969) 953.
14 B. F. G. Johnson, J. Lewis and M. S. Subramanian, *J. Chem. Soc., A*, (1968) 1993.
15 R. B. King, *J. Organometal Chem.*, 14 (1968) P 19.
16 R. B. King, P. M. Treichel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83 (1961) 3593.
17 P. A. Wadsworth and K. W. Barnett, unpublished.
18 M. I. Bruce, in F. G. A. Stone and R. West (Eds.), *Advan. Organometal Chem.*, Vol. 6, Academic Press, New York, 1968, p. 273.
19 R. I. Reed and F. M. Tabrizi, *Appl. Spectrosc.*, 17 (1963) 124.
20 A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, 51 (1964) 3847.
21 S. Otsuka and M. Rossi, *J. Chem. Soc., A*, (1968) 2630.
22 C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, 89 (1967) 5144.
23 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
24 E. O. Fischer and H. Werner, *Tetrahedron Lett.*, (1961) 17; M. Dubeck and A. H. Filbey, *J. Amer. Chem. Soc.*, 83 (1961) 1257; K. W. Barnett, F. D. Mango and C. A. Reilly, *J. Amer. Chem. Soc.*, 91 (1969) 3387.
25 M. D. Rausch, Y. F. Chang and H. B. Gordon, *Inorg. Chem.*, 8 (1969) 1355.
26 R. B. King, *Appl. Spectrosc.*, 23 (1969) 148.