CHEMISTRY LETTERS, pp. 1119-1120, 1972. Published by the Chemical Society of Japan

THE DECARBONYLATION OF METHANOL WITH Ni(0) COMPLEX

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$Ni(CO)(PPh_3)_3$ was prepared by treating $Ni(COD)_2$ [COD=1,5-cyclooctadiene] with methanol in the presence of triphenylphosphine and a conjugated diene such as isoprene. The conjugated diene, which was a necessary component of the formation of the complex, was hydrogenated with the residual fragment from methanol, <u>e</u>.<u>g</u>. hydrogen. Together with the complex formation reaction, addition of methanol to the diene was accomplished.

It has been reported that tertiary phosphine transition-metal halide complexes on treatment with alcohols, usually in the presence of base, give carbonyl complexes.$^{1)}$ However, those transition-metal complexes reported are of the second or third row of the periodic table and those of the first row have, to our best knowledge, not been reported yet. We now report the formation of the complex $Ni(CO)(PPh_3)_3$ by treating $Ni(COD)_2$ [COD=1,5-cyclooctadiene] with methanol in the presence of triphenylphosphine and a conjugated diene such as isoprene. Adduct of methanol with the conjugated diene is obtained together with the carbonyl complex. The results were listed in Table 1.

$$Ni(COD)_2 + 3\ PPh_3 + CH_3OH \xrightarrow[\text{diene}]{\text{conjugated}} Ni(CO)(PPh_3)_3 + \text{methanol-diene adduct}$$

The infrared spectrum of the complex showed a very strong peak at 1927 cm^{-1} assignable to C≡O stretching frequency and the elemental analysis of the complex was in accord with the formula $Ni(CO)(PPh_3)_3$ [Found: C;76.05 H;5.37 %. Calcd. for $C_{55}H_{45}P_3ONi$: C;75.62 H;5.19 %].

The reaction of $Ni(COD)_2$ with methanol-diene adduct instead of methanol did not yield the carbonyl complex. The carbon monoxide ligand was derived from methanol directly, and the conjugated diene was hydrogenated with the residual fragment from methanol, <u>e</u>.<u>g</u>. hydrogen. The hydrogenated products were monoenes, which were confirmed by gas chromatography. It was shown experimentally that a conjugated diene was a necessary component of the formation of the carbonyl complex by the decarbonylation of methanol. Ethanol or benzyl alcohol failed to give the carbonyl complex.

The addition product of methanol to a conjugated diene obtained was mainly Markovnikov type. When diene was isoprene, the reaction proceeded as follows.

$$CH_3OH + CH_2{=}C(CH_3){-}CH{=}CH_2 \xrightarrow[PPh_3]{Ni(COD)_2} CH_2{=}C(CH_3){-}CH(OCH_3){-}CH_3$$

The NMR spectrum of the product showed the absorption at τ 8.90(CH_3-$\overset{|}{\underset{|}{C}}$-, 3H, d), 8.43($CH_3$-$\overset{|}{C}$=, 3H, m), 6.95($CH_3$-O-, 3H, s), 6.40(H-$\overset{|}{\underset{|}{C}}$-, 1H, m), 5.25(H-$\underset{|}{C}$=$\underset{|}{C}$-Me, 1H, m), and 4.59(H-$\overset{|}{C}$=$\underset{|}{C}$-Me, 1H, m).

Table 1. Interaction of $Ni(COD)_2$ with CH_3OH in the presence of PPh_3 and olefin
$Ni(COD)_2$=6.60-8.80 × 10^{-4}mol, Olefin 3 ml, CH_3OH 8 ml, 100°C, 2.5 hr.

PPh_3/Ni (molar ratio)	Olefin	Yield of $Ni(CO)(PPh_3)_3$ (%)[a]	Yield of methanol-diene adduct (%)[b]
3	-	-	-
3	1-pentene	-	-
3	1,5-cyclooctadiene	-	-
3	1,3-cyclooctadiene	-	-
3	butadiene[c]	45	+
3	1,3-pentadiene	64	+
0	isoprene	-	-
1	isoprene	27	2.2
2	isoprene	58	10.7
3	isoprene	73	10.7
4[d]	isoprene	37	13.4

a) based on the critical component, b) based on isoprene, c) 90°C,
d) $Ni(PPh_3)_4$ complex was used

References

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(Received September 11, 1972)