Formation of the Nickela-cyclic Amide Complex 1-Tricyclohexylphosphino-4-methyl-1,2-azanickelacyclopentan-3-one by the Reaction of Methacrylamide with Bis(cyclo-octadiene)nickel in the Presence of Tricyclohexylphosphine

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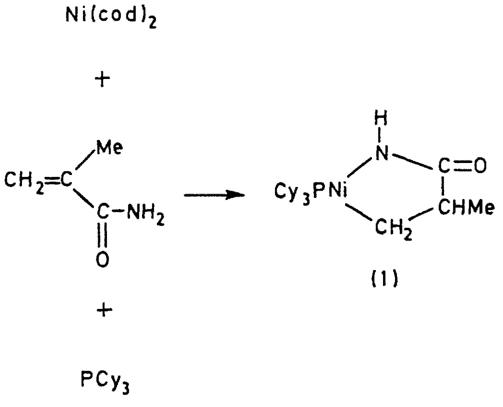
Summary The reaction of bis(cyclo-octadiene)nickel with methacrylamide in the presence of tricyclohexylphosphine (PCy_3) gives a nickela-cyclic amide complex $(\mathrm{PCy_3})\overline{\mathrm{NiNHCOCHMeC}}\mathrm{H_2}$ (**1**), which affords 3-methylsuccinimide on reaction with CO.

THE reaction of olefins with transition metal compounds generally affords π-type complexes[1] and formation of other types of complexes such as a metallacyclic complex[2] is exceptional. We now report the formation of a nickela-cyclic amide by the reaction of methacrylamide (maa) with bis(cyclo-octadiene)nickel [$Ni(cod)_2$] in the presence of tricyclohexylphosphine (PCy_3).

When a mixture of Ni(cod)$_2$ (2·1 mmol), maa (4·0 mmol), and PCy$_3$ (2·1 mmol) in tetrahydrofuran (7 ml) was stirred at room temperature for 2 h, a yellow-green precipitate (580 mg) was obtained which was recrystallized from toluene to give yellowish-green crystals of the nickelacyclic amide complex (**1**) [reaction (1)].†

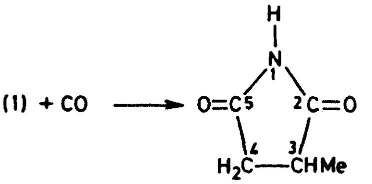


(1)

(1)

The i.r. spectrum (KBr) of (**1**) is quite different from those of π-type αβ-unsaturated amide complexes of Ni such as Ni(π-acrylamide)$_2$(bpy)[3] (bpy = 2,2′-bipyridyl) and Ni(π-maa)(PPh$_3$)$_2$ (**2**) (*vide infra*) showing a singlet ν(N–H) absorption at 3400 cm^{-1} and only one sharp strong band at 1568 cm^{-1} which is characteristic of cyclic amides.[4] The ^{1}H n.m.r. spectrum (C$_6$D$_6$) of (**1**) shows a proton peak at δ 5·90, assignable to NH, which is absent if [*NN*-^{2}H$_2$]maa is used as the starting material. Assignment of other peaks was not possible owing to overlapping of the CH, CH$_2$, and CH$_3$ signals in the metallacycle and those of the PCy$_3$-protons. The ^{1}H n.m.r. spectrum (C$_6$H$_6$) of the π-type complex (**2**) shows an NH$_2$ peak (2H) at δ 4·23.

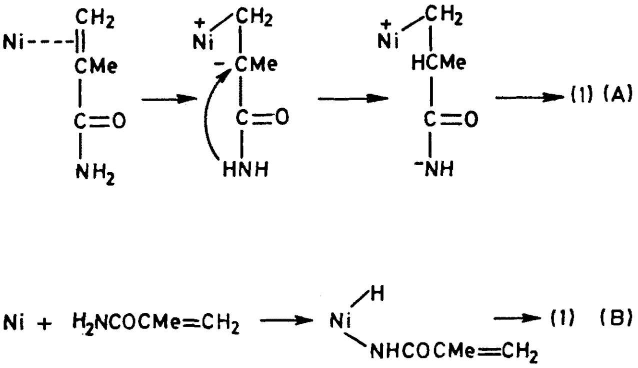
Addition of excess of PCy$_3$ to an ethereal solution of (**1**) did not lead to the liberation of maa. Complex (**1**) reacted instantly with CO at room temperature to give 3-methylsuccinimide quantitatively [reaction (2)]. It is known that metallacyclic compounds give cyclic ketones on reaction with CO.[5] The reaction of CO with [^{2}H$_2$]-(**1**), prepared by using [*NN*-^{2}H$_2$]maa, gave 3-methyl[1,3-^{2}H$_2$]succinimide (n.m.r., i.r.), supporting the metallacyclic structure. The Co$_2$(CO)$_8$-catalysed preparation of 3-methylsuccinimide from maa and CO under severe conditions has been reported[6] and the result obtained here suggests the formation of an intermediate cobaltacyclic amide under these catalytic conditions.



(2)

In contrast to the reaction of Ni(cod)$_2$ with maa in the presence of PCy$_3$, a similar reaction in the presence of triphenylphosphine gave yellow needles of a normal π-type complex Ni(π-maa)(PPh$_3$)$_2$ (**2**) in 82% yield,† the i.r. spectrum (KBr) of which shows amide bands at 1645 and 1580 cm^{-1}. The reaction of (**2**) with CO gave Ni(CO)$_2$(PPh$_3$)$_2$ and maa quantitatively.

The formation of (**1**) seems to proceed through an intramolecular Michael reaction type shift of H from NH$_2$ to the α-carbon in a polarized canonical structure of an Ni–maa π-complex (Scheme, A) or an oxidative addition of the N–H bond of maa to Ni (Scheme, B).



Scheme

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† Satisfactory elemental analyses were obtained.

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