Synthesis and nuclear magnetic resonance solution studies of zerovalent nickel–carbonyl–dppm complexes

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Abstract

Three nickel–carbonyl–dppm complexes, $Ni(CO)_2(\eta^1\text{-dppm})_2$, $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$ and $Ni_2(\mu\text{-dppm})_2(CO)_4$ have been prepared by minor modifications of a single synthetic procedure. The complexes were characterized in the solid state by IR analysis and in solution by ^{31}P NMR analysis. In solution, at 25 °C, $Ni(CO)_2(\eta^1\text{-dppm})_2$ rearranges to initially form $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$, CO and dppm followed by the subsequent reaction of $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$ with CO to yield $Ni_2(\mu\text{-dppm})_2(CO)_4$. Carbon monoxide gas uptake measurements were conducted to determine the extents of the interconversions of the three nickel–carbonyl–dppm complexes at 25 °C and 700 torr. Reaction of CO with $Ni(CO)_2(\eta^1\text{-dppm})_2$ yielded a fourth zerovalent complex, $Ni(CO)_3(\eta^1\text{-dppm})$.

Introduction

$Ni(CO)_2(\eta^1\text{-dppm})_2$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) has recently been used as a starting material for the syntheses of homobimetallic nickel [1] and heterobimetallic nickel–platinum [2] and nickel–palladium [3] complexes. In an attempt to optimize the yields of our nickel–palladium compound [3], we found that $Ni(CO)_2(\eta^1\text{-dppm})_2$ [2] displayed some interesting solution characteristics. In addition, it was observed that during the synthesis of this complex, depending on the reaction conditions, several other zerovalent nickel–carbonyl–dppm complexes were obtained, $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$ (**2**) [4], $Ni_2(\mu\text{-dppm})_2(CO)_4$ (**3**) [5] and $Ni(CO)_3(\eta^1\text{-dppm})$ (**4**) [5]. These observations initiated a detailed investigation into the formation and solution behavior of these compounds. The results of some of these investigations are reported in this paper.

Experimental

All experiments were performed under a CO or N_2 atmosphere. $^{31}P\{^1H\}$ NMR (81 MHz) were recorded on a Bruker AC/E-200 FT-NMR spectrometer in C_6D_6. Chemical shifts were referenced to 85% H_3PO_4. IR spectra were obtained between 4000 and 400 cm^{-1} on a Nicolet-10DX FT-IR spectrometer using KBr pellets for solids and NaCl solution cells for liquids.

$[Ni(H_2O)_6]Cl_2$ (1.0 g, 4.21×10^{-3} mol) was added to 40 ml methanol resulting in a lime green solution. Carbon monoxide was bubbled through this solution for 10 min. From this point on, the formation of three different nickel complexes **1**, **2** or **3** could be achieved depending on the specific reaction conditions. Satisfactory elemental analyses were obtained for all compounds.

$Ni(CO)_2(\eta^1\text{-dppm})_2$ (1)

Complex **1** was obtained by adding a solution of dppm (5.0 g, 0.013 mol) in toluene (45 ml) to the lime green nickel solution with the dppm to nickel ratio of three to one. The resulting deep maroon solution was reduced by slow addition of $NaBH_4$ (1.32 g, 0.034 mol), resulting in a light brown suspension. The reaction mixture was immediately put on ice, 50 ml of deoxygenated hexanes were added and the suspension was placed in the refrigerator for 12 h. A white solid which

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precipitated, was filtered and dried *in vacuo*. Typical yields ranged from 92 to 95%.

$Ni_2(\mu$-dppm$)_2(\mu$-CO$)(CO)_2$ (2)

Complex **2** was obtained by addition of a solution of dppm in toluene to the nickel solution with a dppm to nickel mole ratio of one to one. The reaction remained under a constant light flow of carbon monoxide. $NaBH_4$ was added over a 5 min period and a yellow solid was precipitated by addition of 40 ml of deoxygenated methanol. The product was washed with methanol and dried *in vacuo*, producing **2** in 50–60% yields.

$Ni_2(\mu$-dppm$)_2(CO)_4$ (3)

Complex **3** was obtained by addition of a solution of dppm in toluene to the nickel solution in a one to one mole ratio. $NaBH_4$ was added over a 5 min period while vigorously bubbling carbon monoxide through the solution for at least 20 min following the addition of $NaBH_4$. Addition of deoxygenated methanol to the reaction mixture afforded a pale yellow precipitate which was filtered and dried *in vacuo*. Typical yields were 60%.

Results and discussion

The reaction between Ni(II) and $NaBH_4$ in the presence of dppm and carbon monoxide leads to the formation of three zerovalent nickel–carbonyl–dppm complexes, $Ni(CO)_2(\eta^1$-dppm$)_2$ (**1**), $Ni_2(\mu$-dppm$)_2(\mu$-CO$)(CO)_2$ (**2**) and $Ni_2(\mu$-dppm$)_2(CO)_4$ (**3**). Compound **1**, a white solid, displays two terminal carbonyl IR bands at 1987 and 1925 cm^{-1}. The ^{31}P NMR spectrum of this compound is characteristic of an AA'XX' spectrum with peaks centered at 23.7 and −25.4 ppm (Fig. 1(a))*. In the solid state, the compound is air stable for weeks while in solution under nitrogen or vacuum, it gradually rearranges to form compounds **2** (23.2 ppm) and **3** (18.8 ppm) as well as free dppm (21.5 ppm) as evidenced by *in situ* solution NMR (Fig. 1(b) and (c)) (eqns. (1) and (2)).

$$2Ni(CO)_2(\eta^1\text{-dppm})_2 \rightleftharpoons Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2 + CO + 2dppm \quad (1)$$

$$Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2 + CO \rightleftharpoons Ni_2(\mu\text{-dppm})_2(CO)_4 \quad (2)$$

The NMR signal of $Ni_2(\mu$-dppm$)_2(\mu$-CO$)(CO)_2$ is not well resolved as it virtually coincides (Fig. 2) with one of the peaks from $Ni(CO)_2(\eta^1$-dppm$)_2$. The order of these reactions was established by observing that the signal of 2 appeared before the signal of 3.

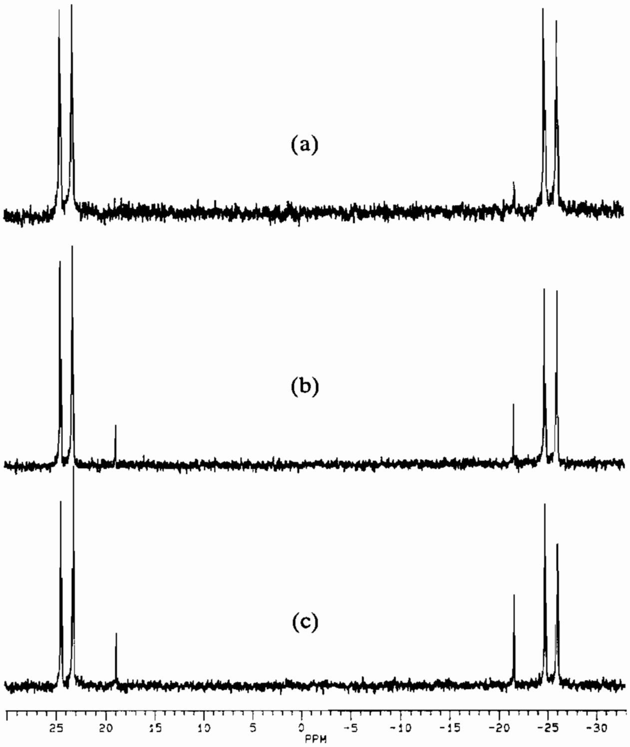

Fig. 1. ^{31}P NMR of $Ni(CO)_2(\eta^1$-dppm$)_2$ in C_6D_6 at 25 °C, (a) 2 min in solution, (b) 5 min in solution, (c) 7 min in solution.

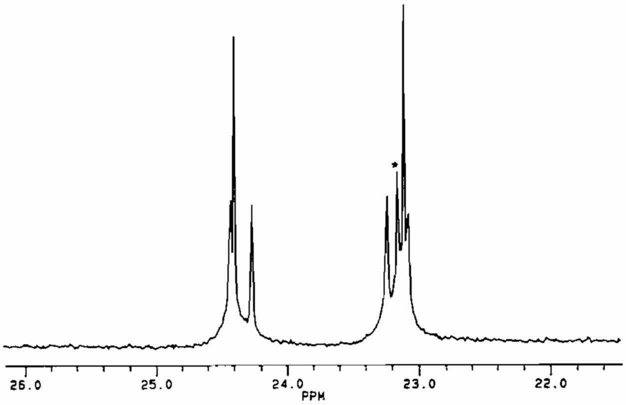

Fig. 2. Expanded ^{31}P NMR of $Ni(CO)_2(\eta^1$-dppm$)_2$ in C_6D_6 at 25 °C. Asterisk (*) denotes $Ni_2(\mu$-dppm$)_2(\mu$-CO$)(CO)_2$ at 23.2 ppm

The overall equation for the reaction is given as (eqn. (3))

$$2Ni(CO)_2(\eta^1\text{-dppm})_2 \rightleftharpoons Ni_2(\mu\text{-dppm})_2(CO)_4 + 2dppm \quad (3)$$

$Ni_2(\mu$-dppm$)_2(\mu$-CO$)(CO)_2$ (**2**), a yellow solid, displays a singlet in the ^{31}P NMR at 23.2 ppm. Its IR

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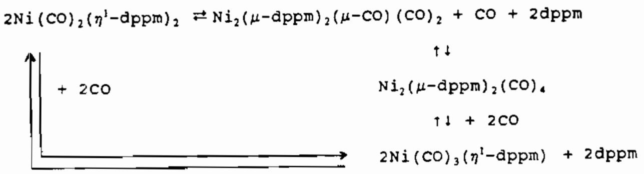
*Resonance due to dppm at 21.5 ppm is always observed as $Ni(CO)_2(\eta^1$-dppm$)_2$ rearranges instantaneously at 25 °C. At −80 °C, the complex is stable and this resonance is absent.



Scheme 1.

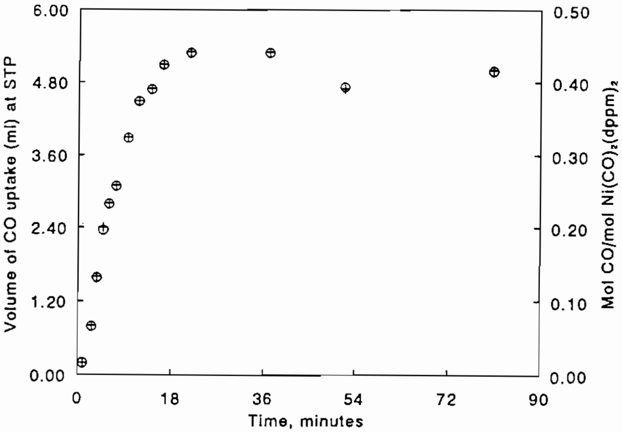


Fig. 3. Carbon monoxide uptake by 0.455 mmol of $Ni(CO)_2(\eta^1\text{-}dppm)_2$ at 25 °C and 700 torr.

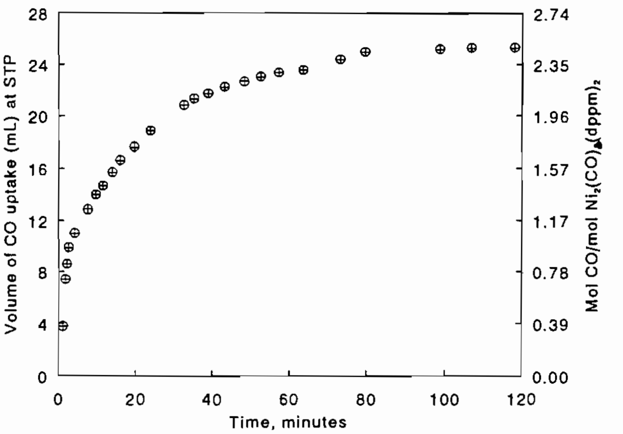


Fig. 4. Carbon monoxide uptake by 0.455 mmol of $Ni_2(\mu\text{-}dppm)_2(\mu\text{-}CO)(CO)_2$ at 25 °C and 700 torr.

spectrum is characterized by two terminal carbonyl bands at 1965 and 1945 cm^{-1} and a bridging carbonyl band at 1784 cm^{-1}. These observations are consistent with previous characterizations of this complex [4]. The complex is stable for several weeks under vacuum and does not decompose in non-chlorinated, non-polar solvents for several hours.

$Ni_2(\mu\text{-}dppm)_2(CO)_4$ (**3**), a pale yellow solid, displays four IR peaks at 2003, 1994, 1944 and 1930 cm^{-1}, all characteristic of terminal CO groups, and a ^{31}P NMR singlet at 18.8 ppm. These observations are consistent with the previously reported characterization of this compound [5]. Complex **3** slowly decomposes under vacuum over several days to yield compound **2** as evidenced by ^{31}P NMR analysis (eqn. (4)).

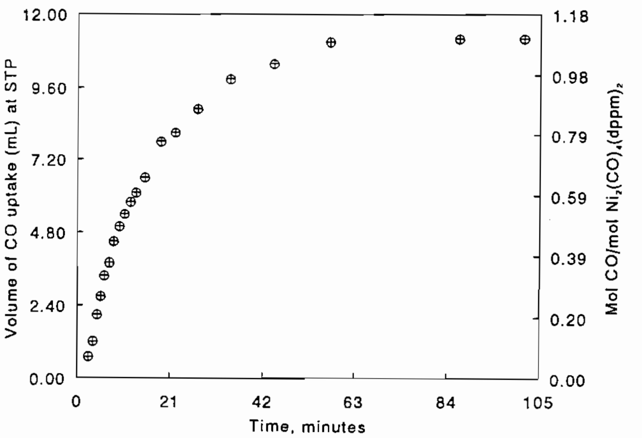


Fig. 5. Carbon monoxide uptake by 0.455 mmol of $Ni_2(\mu\text{-}dppm)_2(CO)_4$ at 25 °C and 700 torr.

$$Ni_2(\mu\text{-}dppm)_2(CO)_4 \rightleftharpoons Ni_2(\mu\text{-}dppm)_2(\mu\text{-}CO)(CO)_2 + CO \quad (4)$$

In solution, the decomposition (eqn. (4)) is much more rapid (1–2 h).

Solution rearrangement of compound **1** to **2** and **3** can be prevented by the addition of free dppm to a solution of **1**, thus shifting the equilibrium of eqn. (1) to the left. Addition of CO to a solution of **1** also prevented the formation of **2** and **3**, but a fourth nickel complex, $Ni(CO)_3(\eta^1\text{-}dppm)$ (**4**), was obtained (eqn. (5)), by a ligand displacement reaction.

$$Ni(CO)_2(\eta^1\text{-}dppm)_2 + CO \rightleftharpoons Ni(CO)_3(\eta^1\text{-}dppm) + dppm \quad (5)$$

This mononuclear, monodentate nickel compound **4** was characterized only by ^{31}P solution NMR (doublet–doublet centered at 22.5 and −24.8 ppm, $J(P\text{–}P) = 124$ Hz) since we were unable to obtain this complex in the solid state. These data are consistent with previous observations of this complex in solution [5]. In solution, when not under a CO atmosphere, compound **4** slowly rearranges to yield first complex **3** (eqn. (6)).

$$2Ni(CO)_3(\eta^1\text{-}dppm) \rightleftharpoons Ni_2(\mu\text{-}dppm)_2(CO)_4 + 2CO \quad (6)$$

followed by the formation of complex **2** (eqn. (4)).

Scheme 1 summarizes the solution interconversions of all nickel–carbonyl–dppm complexes.

A series of CO gas uptake experiments was performed to quantitatively establish the extents of the various equilibria shown in Scheme 1. Gas uptake experiments by complexes **1**, **2** and **3** were performed at 25 °C and a pressure of 700 torr.

Reaction of **1** with CO (eqn. (5)) yielded a CO uptake of 0.41 mol per mole of $Ni(CO)_2(\eta^1\text{-dppm})_2$ indicative of a 41% conversion of starting material to product **4** (Fig. 3).

The expected CO uptake of **2** to yield **3** is 1 mol of CO per mole of complex (eqn. (2)), however the experimentally observed uptake corresponds to 2.5 mol of CO per mole of complex (Fig. 4), clearly showing that **3** adds CO to yield **4** (reverse of eqn. (4)). ^{31}P NMR data confirmed that both complexes **3** and **4** were formed during the course of this reaction.

Finally, reaction of **3** with CO yielded an uptake of 1.1 mol of CO per mole of starting complex (Fig. 5) (eqn. (7)) indicative of a 55% conversion of reactant

$$Ni_2(\mu\text{-dppm})_2(CO)_4 + 2CO \rightleftharpoons 2Ni(CO)_3(\eta^1\text{-dppm}) \quad (7)$$

to product. This observation is in excellent agreement with the previously reported CO uptake of **3** under similar reaction conditions [5]. When reacting **3** with a higher pressure of CO (2.5 atm), **4** was obtained in 100% yield as evidenced by solution NMR. No $Ni(CO)_4$ was formed as that would have yielded free dppm which was not observed.

Conclusions

The studies of the formation of mononuclear and binuclear nickel complexes have shown that four different complexes (two with monodentate dppm ligands and two with bridging bidentate dppm ligands) can be synthesized by making relatively minor modifications to the reaction conditions of a general synthetic procedure.

Solution studies and gas uptake measurements have shown that a delicate equilibrium exists between the four species at room temperature and atmospheric pressure.

Acknowledgements

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References

1 L. Manojlovic-Muir, K. W. Muir, W. M. Davis, H. A. Mirza and R. J. Puddephatt, *Inorg. Chem., 31* (1992) 904.

2 D. G. Holah, A. N. Hughes, V. R. Magnuson, H. A. Mirza and K. O. Parker, *Organometallics, 7* (1988) 1233.

3 S. Schreiner, M. M. Setzer and T. N. Gallaher, *Inorg. Chim. Acta, 188* (1991) 131.

4 (a) D. G. Holah, A. N. Hughes, H. A. Mirza and J. D. Thompson, *Inorg. Chim. Acta, 126* (1987) L7; (b) Z. Z. Zhang and H. K. Wang, *J. Organomet. Chem., 347* (1988) 269; (c) J. K. Gong and C. P. Kubiak, *Inorg. Chim. Acta, 162* (1989) 19.

5 J. A. Osborn, G. G. Stanley and P. H. Bird, *J. Am. Chem. Soc., 110* (1988) 2117.