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LETTER

Synthesis, characterization and reactivity of the heterodinuclear complex [NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$]

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Bimetallic complexes of transition metals bridged by $Ph_2PCH_2PPh_2$ (dppm) have been extensively studied [1]. While the majority of these studies focused on the synthesis of homonuclear complexes [1], Shaw and co-workers have prepared numerous dppm-bridged heteronuclear complexes [2]. Recently, the first binuclear complexes containing Ni–Pd [3] and Ni–Pt [3, 4] bonds have been reported. Bimetallic complexes bridged by dppm have great potential in catalysis [5] and, in particular, it was recently shown that $Pt_2(\mu\text{-dppm})_3$ catalyzed the hydrogenation of carbon dioxide in the presence of dimethylamine under unprecedented mild conditions [6]. These results prompted us to explore the synthesis of similar complexes and to study their potential as catalyst precursors for hydrogenation reactions. Some results of these investigations are reported in this letter.

Experimental

All manipulations were performed under a N_2 atmosphere using Schlenk techniques. $^{31}P\{^1H\}$ NMR (81 MHz) spectra were recorded on a Bruker AC/E-200 FT-NMR spectrometer with chemical shifts referenced to 85% H_3PO_4. IR spectra were recorded on a Mattson 4020 FT-IR spectrometer.

$Ni(CO)_2(\eta^1\text{-dppm})_2$ (0.270 g, 0.305 mmol) was dissolved in 75 ml of toluene under N_2. The initially colorless solution slowly turned deep yellow. $PdCl_2(PhCN)_2$ (PhCN = benzonitrile) (0.117 g, 0.310 mmol) was added to the reaction mixture, yielding a deep blue solution. Slow addition of 150 ml hexanes afforded a blue precipitate. The solid was filtered, washed with methanol and toluene, and dried *in vacuo*. Typical yields ranged from 75–85%.

Results and discussion

Reaction between $Ni(CO)_2(\eta^1\text{-dppm})_2$ (**1**) and $PdCl_2(PhCN)_2$ in toluene with the reagents in a 1:1 molar ratio yields [NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$] (**2**). *Anal.* Calc. for $C_{51}H_{44}Cl_2NiPdOP_4$: C, 59.31; H, 4.26; Cl, 6.87. Found: C, 58.59; H, 4.62; Cl, 7.57%. Energy dispersive X-ray spectroscopic analysis of the crystals established the presence of nickel, palladium, phosphorus and chlorine.

The reaction involves initial conversion of the monodentate dppm nickel complex to two bimetallic compounds, $Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2$ (**3**) and $Ni_2(\mu\text{-dppm})_2(CO)_4$ (**4**) (eqns. (1) and (2)).

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

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

$^{31}P\{^1H\}$ NMR spectra obtained from the solution before addition of $PdCl_2(PhCN)_2$ show chemical shifts attributable to the starting material (23.5 ppm, triplet, and −25.8 ppm, triplet, characteristic of an AA'XX' spectrum) [4], complex **3** (22.9 ppm) [7], complex **4** (18.4 ppm) [8] as well as free dppm (−21.9 ppm). Whether it is complex **3** (eqn. (3)) and/or complexes **1** or **4** which react with $PdCl_2(PhCN)_2$ to yield the title compound has not been established. The overall equation for the reaction can be depicted as follows (eqn. (4)):

$$Ni_2(\mu\text{-dppm})_2(\mu\text{-CO})(CO)_2 + 2PdCl_2(PhCN)_2 + 2dppm \longrightarrow 2[NiPd(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2] + 4PhCN + CO \quad (3)$$

$$Ni(CO)_2(\eta^1\text{-dppm})_2 + PdCl_2(PhCN)_2 \longrightarrow [NiPd(\mu\text{-dppm})_2(\mu\text{-CO})Cl_2] + 2PhCN + CO \quad (4)$$

The solid state IR spectrum of **2** shows a single stretching vibration at 1785(s) cm^{-1} indicating the presence of only a bridging carbonyl group. The location of this band in the IR spectrum is similar to the value (1754 cm^{-1}) reported for a structurally

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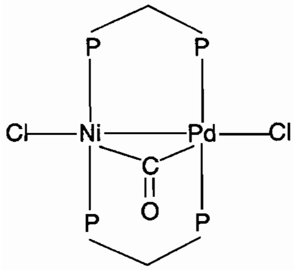

Fig. 1. Proposed structure of [NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$].

analoguous Ni–Pt compound [4]. In solution (CH_2Cl_2), the ν(CO) stretching vibration is shifted to 1787 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 is of the AA'BB' type. Peaks are centered at 26.9 and 19.1 ppm with the following indirect coupling constants: $^2J(AA') = 416$ Hz, $^2J(BB') = 103$ Hz, $^2J(AB) = 191$ Hz and $^4J(AB') = -6.2$ Hz (chemical shifts and coupling constants were obtained by computer simulation using PANIC). The chemical shift values agree well with those of the palladium dimer (19.1 ppm) [9] and the nickel dimer (21.8 ppm) [10]. On the basis of these data, the resonance at 26.9 ppm is assigned to the phosphorus atoms coordinated to nickel and the resonance at 19.1 ppm is assigned to the phosphorus atoms coordinated to palladium.

Compound **2** is insoluble in most polar solvents, sparingly soluble in aromatic hydrocarbons and slightly more soluble in chlorinated hydrocarbons, DMF and DMSO. The proposed formulation and the assignment of a structure like that shown in Fig. 1 was made based on elemental analysis, spectroscopic data and the known crystal structure of the analogous Ni–Pt complex [4].

In the solid state, the complex is air-stable for weeks, while it is very air-sensitive in solution. A dichloromethane solution of **2** in air gradually changes from its characteristically deep blue color to an orange color. $^{31}P\{^1H\}$ NMR analysis of the solution exposed to air indicates that the compound decomposes to yield $PdCl_2$(dppm) (−54.0 ppm), Pd_2(μ-dppm)$_2Cl_2$, (−2.3 ppm), Pd_2(μ-dppm)$_2$(μ-CO)Cl_2 (19.1 ppm), dppm oxide (25.3 ppm) as well as two unidentified species (11.9 ppm and 24.8 ppm) which are believed to be nickel complexes.

[NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$] is fairly stable towards loss of CO. Vigorous N_2 bubbling through a solution of **2** in dichloromethane for an extended period of time did not result in the loss of carbon monoxide. Upon heating the compound in the solid state in air at 125 °C, the complex gradually changes color from blue to green. This change in color is accompanied by a loss of the bridging carbonyl as evidenced by IR spectroscopy.

Further studies of the complex with regard to the activation of small molecules are in progress.

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