Bimetallic Systems. Part 18.[1] Nickel(II)–Mercury(II) Acetylide Complexes containing Bridging $Ph_2PCH_2PPh_2$ Ligands

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Treatment of $[Ni(dppm\text{-}P)_2X_2]$ (dppm = $Ph_2PCH_2PPh_2$; X = Cl, Br, or I) with $Hg(C{\equiv}CR)_2$ (R = Ph or *p*-tolyl) in benzene or dichloromethane solution gives the yellow complexes $[(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgX_2]$. Treatment of $[Ni(dppm\text{-}P)_2Cl_2]$ with two equivalents of $[Au(PPh_3)(C{\equiv}CR)]$ gives what appears to be $[(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2Au]Cl$, characterized by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy, but too labile to be isolated pure. Attempts to synthesize other Ni^{II}-containing heterobimetallic complexes are also described.

There have been very extensive studies on the co-ordination chemistry of Pt^{II} and Pd^{II} with dppm ($Ph_2PCH_2PPh_2$) in mononuclear and homo- or hetero-binuclear complexes.[2–4] In contrast, Ni^{II}–dppm chemistry has been largely restricted to mononuclear species, characterized principally by electronic spectroscopy: complexes have included $[Ni(dppm\text{-}P)_2X_2]$ (X = Cl, Br, or I) for which in the solid state dppm is monodentate,[5,6] $[Ni(dppm\text{-}PP')X_2]$,[7,8] and $[Ni(dppm\text{-}PP')_2]Y_2$[9] (Y = a non-co-ordinating anion such as NO_3, ClO_4, or BPh_4). Discrete, five-co-ordinate complexes $[Ni(dppm\text{-}PP')_2X]Y$ have also been synthesized.[8] In contrast, Pd^{II} and Pt^{II} mononuclear complexes are restricted to $[M(dppm\text{-}PP')_2]X_2$ and $[M(dppm\text{-}PP')X_2]$.[10,11]

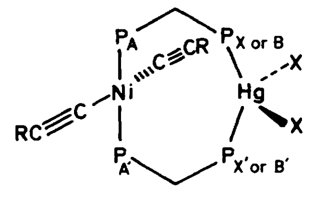
A number of Ni^I complexes of dppm, which appear to be binuclear, have been made recently by BH_4^- or BH_3CN^- reduction of Ni^{II} salts in the presence of dppm,[12,13] but these are very labile and have not been fully characterized. Similarly, the structure of the apparently binuclear $[\{Ni(dppm)(NCS)_2\}_2]$ is uncertain.[7,8] The heterobimetallic complex $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-dppm})(\mu\text{-SPh})Mo(CO)_4]$ has been prepared from $[Ni(\eta^5\text{-}C_5H_5)(dppm\text{-}P)(SPh)]$ and $[Mo(CO)_4(nbd)]$ {nbd = norbornadiene(bicyclo[2.2.1]hepta-3,5-diene)}.[14] More recently, the complex $[Ni_2(\mu\text{-CNMe})(\mu\text{-dppm})_2(CNMe)_3][PF_6]_2$ has been synthesized and found to have an unusual structure, with the Ni atoms in surprisingly different environments.[15]

While complexes of the type $[(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2]$ (R = Ph or *p*-tolyl) are readily prepared from $[Pt(dppm\text{-}PP')_2]Cl_2$ and $Hg(C{\equiv}CR)_2$ in benzene, and are stable complexes with sharp, well resolved AA′XX′- or AA′BB′-type spectra,[16] the corresponding Pd^{II} complexes decompose to unidentified products at room temperature and are generated in solution at −20 °C.[17] We now wish to report that, somewhat surprisingly, complexes of the type $[(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgX_2]$ can be synthesized at room temperature and have moderate stability as solids.

Results and Discussion

Treatment of red-purple $[Ni(dppm\text{-}P)_2X_2]$ (X = Cl, Br, or I), in benzene or dichloromethane, with $Hg(C{\equiv}CR)_2$ (R = Ph or *p*-tolyl) gave orange solutions from which yellow solids were isolated by precipitation with methylcyclohexane (X = Br), ethanol (X = Cl), or methanol (X = I) (see Experimental section). These solids are formulated as $[(RC{\equiv}C)_2Ni(\mu\text{-dppm})HgX_2]$ [R = Ph, X = Cl (**1a**), Br (**2**), or I (**3**); R = *p*-tolyl, X = Cl (**1b**)] on the basis of (*i*) elemental analysis (C, H, and X), (*ii*) i.r. spectra, which show a weak band at *ca.* 2 080 cm^{-1} [$\nu(C{\equiv}C)$] typical of complexes of the type *trans*-$[Ni(PR_3)_2(C{\equiv}CR)_2]$[18] and, most importantly (*iii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, which showed AA′BB′ or AA′XX′ spin systems,

Table. $^{31}P\text{-}\{^1H\}$ N.m.r. data[a]



Complex	θ/ °C	Spin system	δP_A/p.p.m.	δP_X (or P_B) p.p.m.	$^1J(Hg\text{-}P_B)$	$^2J(P_A\text{-}P_{A'})$/ Hz	$^2J(P_X\text{-}P_{X'})$[b]/ Hz	'N'	
								$^2J(P_A\text{-}P_X)$/Hz	$^4J(P_A\text{-}P_{X'})$/Hz
(**1a**)[c]	−60	AA′BB′	22.6	21.0	5 678	346	126	69	−2
(**1b**)[c]	−50	AA′BB′	22.3	20.1	5 645	329	112	69	−1
(**2**)[c]	−60	AA′XX′	23.3	16.8	5 265	335	31	69	−2
(**3**)[d]	−70	AA′XX′	23.8	4.6	4 346	—	—	66	
(**4a**)	−40	AA′XX′	21.6	33.2	—	—	—	64	
(**4b**)[d]	−40	AA′BB′	21.5	32.5	—	—	—	—	

[a] Measured in CD_2Cl_2 solution at 162 MHz, unless stated otherwise; δ values ±0.1 p.p.m., *J* values ±3 Hz. [b] Or $^2J(P_B\text{-}P_{B'})$. [c] These values were obtained using the PANIC computer simulation program. 'N' values were measured directly from the spectrum. See Figure. 'N' = $^2J(P_A\text{-}P_X) + {}^4J(P_A\text{-}P_{X'})$. [d] At 40.3 MHz.

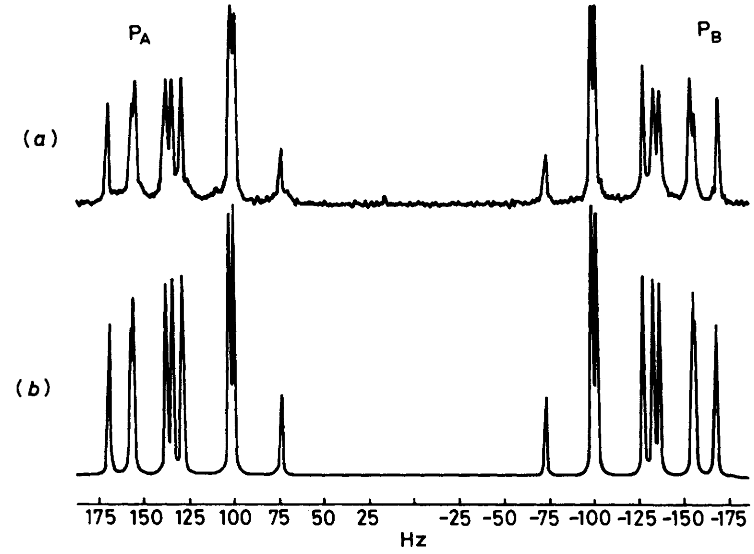


Figure. (*a*) Observed ^{31}P-{^{1}H} n.m.r. spectrum of [$(PhC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgCl_2$] (**1a**) at 162 MHz, excluding the satellites due to $^{1}J(^{199}Hg-^{31}P_B)$ coupling. Three-bond coupling $^{3}J(^{199}Hg-^{31}P_A)$ was not observed. In complexes of type [$(RC{\equiv}C)_2Pt(\mu\text{-dppm})_2HgCl_2$] $^{3}J(^{199}Hg-^{31}P)$ is too small to observe.[16] The centre of the resonance pattern, at 0 Hz, is at +21.80 p.p.m. from 85% H_3PO_4. (*b*) Calculated (PANIC) 162-MHz n.m.r. spectrum of [$(PhC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgCl_2$] (**1a**) using the parameters given in the Table. Satellites due to $^{1}J(^{199}Hg-^{31}P_B)$ coupling are not included. Since the agreement between the calculated and observed pattern for P_A is good, it suggests that three-bond coupling, $^{3}J(^{199}Hg-^{31}P_A)$, is not zero but is sufficient to broaden out the resonances of P_A in the 17% of the complex containing ^{199}Hg: effectively this part of the pattern appears as background

as previously observed for analogous Pt^{II} complexes,[17] with satellites due to coupling with ^{199}Hg (17% abundance). The spectra were broad and ill-defined at room temperature but well resolved at −30 (X = Cl or Br) or −70 °C (X = I), in contrast to the Pt^{II} complexes, which show sharp lines at room temperature. The broadness of the spectra of the Ni–Hg complexes may be due to Hg exchange. The iodide complex [$(PhC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgI_2$] (**3**), which was prepared at −20 °C, is much less stable than the corresponding chloride or bromide complexes and black solids appear in its dichloromethane solutions in less than 10 min at room temperature. The ^{31}P-{^{1}H} n.m.r. data are given in the Table and part of the ^{31}P-{^{1}H} n.m.r. spectrum of [$(PhC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgCl_2$] (**1a**) is shown in the Figure, together with a calculated spectrum. The ^{1}H or ^{1}H-{^{31}P} n.m.r. spectra were generally uninformative (see Experimental section) with broad resonances for the dppm methylene protons, except in the case of [$(p\text{-}MeC_6H_4C{\equiv}C)_2Ni(\mu\text{-dppm})_2HgCl_2$] (**1b**), for which P–H coupling could be observed, the virtual quintet [apparent *J*(PH) 4 Hz] being due to strong P–P coupling in *trans*-phosphine complexes of this type.

The complexes of type [$(RC{\equiv}C)_2M(\mu\text{-dppm})_2HgCl_2$] (M = Pd or Pt) are useful precursors to heterobimetallic compexes of M with d^8 or d^6 metals, either by transmetallation[16] or *via* [$M(\text{dppm-}P)_2(C{\equiv}CR)_2$], generated by demercuration using Na_2S[17] and subsequent treatment with a labile d^8- or d^6-metal complex. We have been unable to generate [$Ni(\text{dppm-}P)_2(C{\equiv}CR)_2$], either by treating [$(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgX_2$] (X = Cl or Br) with Na_2S at −30 °C, or directly by treating [$Ni(dppm)_2$][BF_4]$_2$ with LiC≡CR or $Hg(C{\equiv}CR)_2$. Attempted transmetallation reactions, using stoicheiometric amounts of [$(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgX_2$] and [$Rh_2Cl_2(CO)_4$], [$Ir(CO)_2Cl(p\text{-}NH_2C_6H_4Me)$], [$Mo(CO)_4(nbd)$], [$PtMe_2(cod)$] (cod = cyclo-octa-1,5-diene) or [$RhCl(PPh_3)_3$] all failed to give heterobimetallic complexes, even at low (−40 °C) temperatures [^{31}P-{^{1}H} n.m.r. evidence]. Treatment of [$Ni(dppm)_2Cl_2$] with these same complexes induced transfer of dppm to form mononuclear complexes with iridium, molybdenum, or platinum, or binuclear (Rh–Rh) complexes with rhodium. These results are probably due to the extreme lability of the Ni^{II} complexes and the relatively low affinity of Ni^{II}, compared with Ir^{I}, Rh^{I}, Pt^{II}, or Mo^{II}, for tertiary phosphines.

While treatment of [$Ni(dppm)_2Cl_2$] with [$Au(PPh_3)Cl$] did not give a heterobimetallic species, when treated with the acetylide complexes, [$Au(PPh_3)(C{\equiv}CR)$],[19] heterobimetallic (Ni–Au) complexes were formed rapidly [^{31}P-{^{1}H} n.m.r. evidence, see Experimental section]. The complexes were probably of the type [$(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2Au$]Cl, by analogy with corresponding platinum complexes,[20] but were very labile and not obtained pure. The ^{31}P-{^{1}H} n.m.r. spectrum of the phenylacetylide complex [$(PhC{\equiv}C)_2Ni(\mu\text{-dppm})_2Au$]Cl (**4a**) was of the AA′XX′ type but the sample was contaminated with a small amount of [$Au(PPh_3)Cl$] and an unidentified impurity: the *p*-tolylacetylide analogue (**4b**) was similarly contaminated.

Experimental

General methods were as previously reported in recent papers from this laboratory.[21] [$Ni(dppm)_2X_2$] (X = Cl, Br, or I)[5,6] and [$Au(PPh_3)(C{\equiv}CR)$] (R = Ph or *p*-tolyl)[19] were prepared by literature methods. As the isolation of analytically pure Hg–Ni complexes is critically dependent on reaction conditions, full details of their preparations are given. N.m.r. spectra were measured in dichloromethane solution.

[$(RC{\equiv}C)_2Ni(\mu\text{-dppm})_2HgCl_2$].—(*i*) R = Ph (**1a**). A solution of [$Ni(dppm)_2Cl_2$] (0.30 g, 0.33 mmol) in dry dichloromethane (12.0 cm^3) was treated with solid $Hg(C{\equiv}CPh)_2$ (0.145 g, 0.36 mmol). The mixture was stirred for 3 min after which EtOH (3 cm^3) was added and the volume reduced slowly *in vacuo* to *ca.* 5 cm^3. This gave the required product which was washed with diethyl ether and dried. Yield: 0.30 g, 69% (Found: C, 59.0; H, 3.9; Cl, 4.9. $C_{66}H_{54}Cl_2HgNiP_4$ requires C, 60.9; H, 4.2; Cl, 5.4%); ν(C≡C) at 2 080w (dichloromethane solution), ν(Hg–Cl) at 240m cm^{-1} (Nujol mull). ^{1}H-{^{31}P} N.m.r.: δ 4.00 p.p.m. (s,

CH_2). The complex was non-conducting in a freshly prepared 1,2-dichloroethane solution.

(*ii*) R = C_6H_4Me-*p* (**1b**). A solution of $[Ni(dppm)_2Cl_2]$ (0.50 g, 0.56 mmol) in benzene (30 cm^3) was treated with $Hg(C{\equiv}CC_6H_4Me\text{-}p)_2$ (0.25 g, 0.58 mmol), dissolved in benzene (30 cm^3). The mixture was then stirred for 2 min, after which the volume was reduced to *ca.* 5 cm^3 under reduced pressure, and ethanol (25 cm^3) added. The resultant yellow solid was filtered off, washed with benzene, and dried *in vacuo*. Yield: 0.34 g, 46% (Found: C, 61.45; H, 4.3; Cl, 4.9. $C_{68}H_{58}Cl_2HgNiP_4$ requires C, 61.4; H, 4.4; Cl, 5.3%); $\nu(C{\equiv}C)$ at 2 080w cm^{-1} (Nujol mull). ^1H-{^{31}P} N.m.r.: δ 3.84 (s, CH_2) and 2.19 p.p.m. (s, Me).

$[(PhC{\equiv}C)_2Ni(\mu\text{-}dppm)_2HgBr_2]{\cdot}CH_2Cl_2$ (**2**).—A solution of $[Ni(dppm)_2Br_2]$ (0.30 g, 0.30 mmol) in benzene (5.0 cm^3) was treated with a solution of $Hg(C{\equiv}CPh)_2$ (0.15 g, 0.32 mmol) in benzene (12 cm^3). The mixture was stirred for 10 min and then concentrated *in vacuo* to 5 cm^3. Methylcyclohexane (10 cm^3) was then added to give the required product (Found: C, 53.6; H, 3.9; Br, 11.0. $C_{67}H_{56}Br_2Cl_2HgNiP_4$ requires C, 54.4; H, 3.8; Br, 10.8%); $\nu(C{\equiv}C)$ at 2 080w cm^{-1} (Nujol mull). ^1H-{^{31}P} N.m.r.: δ 3.99 [s, PCH_2P, $^3J(Hg\text{-}H)$ 75 Hz].

$[(PhC{\equiv}C)_2Ni(\mu\text{-}dppm)_2HgI_2]$ (**3**).—A solution of $Hg(C{\equiv}CPh)_2$ (0.35 g, 0.32 mmol) in CH_2Cl_2 (5.0 cm^3) at −20 °C was added to a solution of $[Ni(dppm)_2I_2]$ (0.35 g, 0.32 mmol) in CH_2Cl_2 (5 cm^3). The product was cautiously precipitated from the yellow solution with MeOH and isolated. Yield: 0.37 g, 78% (Found: C, 54.2; H, 3.6; I, 17.15. $C_{66}H_{54}HgI_2NiP_4$ requires C, 53.4; H, 3.7; I, 17.1%); $\nu(C{\equiv}C)$ at 2 080w cm^{-1} (Nujol mull).

$[(PhC{\equiv}C)_2Ni(\mu\text{-}dppm)_2Au]Cl$ (**4a**).—$[Ni(dppm)_2Cl_2]$ (0.045 g, 0.05 mmol) was added to a solution of $[Au(PPh_3)(C{\equiv}CPh)]$ (0.056 g, 0.1 mmol) in dichloromethane (1.5 cm^3) at *ca.* 20 °C. After 10 min the solution was evaporated to dryness and the residue triturated with benzene, to give the product as a yellow powder. Yield: 0.06 g, 90%. The product was contaminated with *ca.* 5% of $[Au(PPh_3)Cl]$ and a few % of another impurity, see Results and Discussion section (Found: C, 59.2; H, 3.9; Cl, 3.4. $C_{66}H_{54}AuClNiP_4$ requires C, 62.8; H, 4.3; Cl, 2.8%); $\nu(C{\equiv}C)$ at 2 090w cm^{-1} (Nujol mull).

$[(p\text{-}MeC_6H_4C{\equiv}C)Ni(\mu\text{-}dppm)Au]Cl$ (**4b**).—This was prepared as for (**4a**), but was not isolated, and characterized only by its ^{31}P-{^1H} n.m.r. spectrum, see Table.

Acknowledgements

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