Journal of Organometallic Chemistry 541 (1997) 277–283

Synthesis and X-ray crystal structures of dimeric nickel(0) and tetrameric copper(I) iodide complexes of 2-diphenylphosphino-3-methylphosphinine [1]

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Received 20 December 1996; accepted 9 January 1997

Abstract

The dimer $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}\mathbf{1})_2]$ **2** has been prepared by two different procedures which involve the reaction of the 2-diphenylphosphino-3-methylphosphinine ligand **1** with either $Ni(COD)_2$ or $NiBr_2 \cdot DME/Zn$ under CO atmosphere. The crystal structure of **2** has been determined by X-ray crystallography. As the analogous dppm complex, **2** adopts a W-frame structure with two bridging ligands **1**, two terminal carbonyl ligands and one bridging carbonyl ligand. An electrochemical study reveals that the electron density in the Ni_2 core is considerably reduced in **2** compared to the dppm complex.

The reaction of **1** with two equivalents of copper iodide yields the tetranuclear complex $[Cu_4(\mu\text{-}I)_2(\mu_4\text{-}I)_2(\mu\text{-}\mathbf{1})_2]$ **3** which has been identified by an X-ray diffraction study. The structure of **3** consists of an octahedron having a square planar Cu_4 base bridged by two ligands **1** and two μ^2-iodo atoms. The most surprising feature of this structure concerns the coordination of the two other iodide atoms respectively located at each apex of the octahedron, which display a face μ^4-face-bridging bonding mode. © 1997 Elsevier Science S.A.

Keywords: Nickel; Carbonyls; Cyclic voltammetry; Copper; μ^4-Iodo; 2-Phosphinophosphinines

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1. Introduction

Bridged $\widehat{PN}$ ligands such as 2-phosphinopyridines play a crucial role in the elaboration of various dinuclear homo- and heterobimetallic complexes [1]. On the other hand, the coordination chemistry of their phosphorus isostructural analogues 2-phosphinophosphinines still remains poorly developed (for synthesis and coordination chemistry of 2-phosphinophosphinines, see for example Ref. [2]).

Recently, in a preliminary investigation of the coordinating properties of these new ligands towards binuclear transition metal carbonyls (Mn(0), Fe(I) and Mo(I)) [3] we have shown that the presence of the strong π-acceptor phosphorus atom of phosphinines (for theoretical investigations of the phosphinine system, see Ref. [4]) allowed the stabilization, contrary to 2-phos-

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[1] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

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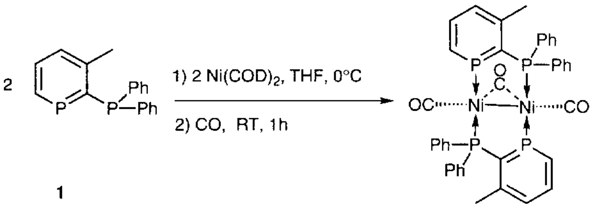
PII S0022-328X(97)00071-5

phinopyridines, of various electron-rich metal–metal bonded complexes. During this study, it also appeared that, in some cases, 2-phosphinophosphinines can have significantly different coordination properties compared with those of bis-diphenylphosphinomethane (dppm). As part of a continuing program of investigation of the structures and properties of transition-metal 2-phosphinophosphinines complexes, we now present some results concerning the interactions of the 2-diphenylphosphino-3-methylphosphinine ligand with nickel(0) and copper(I) centres.

2. Results and discussion

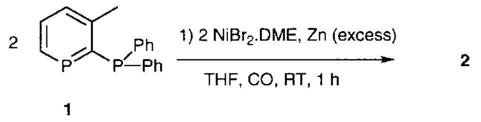
2.1. Synthesis and X-ray structure of the [$Ni_2(\mu$-$CO)(CO)_2(\mu$-$1)_2$] complex (2) (1 = 2-diphenylphosphino-3-methylphosphinine)

Two procedures are available for the synthesis of complex **2**. The first one is identical to that used for the analogous dppm complex [5]. The reaction of $Ni(COD)_2$ with an equimolar amount of phosphinine **1** in THF under CO atmosphere affords **2** with a 60% yield (Eq. (1)).



(1)

The second procedure, which gave **2** with an identical yield, involves the reduction of the $NiBr_2 \cdot DME$ complex with excess zinc under CO atmosphere with one equivalent of ligand **1** (Eq. (2)).



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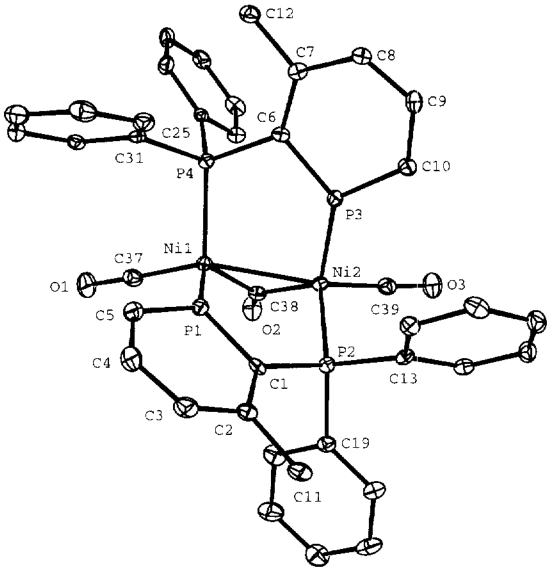


Fig. 1. ORTEP drawing of the molecular structure of complex [$Ni_2(\mu$-$CO)(CO)_2(\mu$-$\mathbf{1})_2$] (**2**) as determined by single crystal X-ray diffraction study with the atomic labelling scheme. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity.

Complex **2**, which was isolated as an orange–red air-stable solid, has been characterized by elemental analysis, infrared and NMR (^1H, ^{31}P, ^{13}C) spectroscopy. The overall molecular geometry of **2** can be easily inferred from its ^{31}P NMR and IR spectra. The presence of two molecules of **1** is confirmed by the analysis of the ^{31}P NMR spectrum which displays a characteristic AA′XX′ pattern. The two multiplets, centred at 241.66 and 29.30 ppm (CD_2Cl_2), are assigned to the phosphinine nucleus and to the diphenylphosphino group respectively. A simulation allowed the determination of all the J(P–P) coupling constants (see Section 3). The infrared spectra of **2** show two ν(CO) (KBr) absorptions at 1982 and 1966 cm^{-1} and another one at 1814 cm^{-1} which confirms the bridging mode of the third carbonyl group. The shift to high frequencies, compared to the dppm complex (1963, 1942, 1770 cm^{-1}), reflects the decrease of π-backbonding induced by the coordination of a better π-accepting ligand (phosphinine) than the PPh_2 group. The W-frame structure of **2**, which crystallizes with three molecules of benzene, has been definitively confirmed by an X-ray

Table 1
Selected bond distances (Å) and angles (°) for complex **2**

Ni(1)–Ni(2)	2.5389(5)	P(1)–C(1)	1.737(3)
Ni(1)–P(1)	2.1748(8)	P(1)–C(5)	1.718(3)
Ni(1)–P(4)	2.2263(8)	C(1)–C(2)	1.414(4)
Ni(1)–C(37)	1.763(3)	C(2)–C(3)	1.395(4)
Ni(1)–C(38)	1.921(3)	C(3)–C(4)	1.389(5)
Ni(2)–P(2)	2.2355(8)	C(4)–C(5)	1.387(4)
Ni(1)–C(38)	1.921(3)	C(1)–P(2)	1.824(3)
Ni(1)–C(37)	1.763(3)	C(37)–O(1)	1.143(4)
C(38)–O(2)	1.166(3)	C(39)–O(3)	1.148(4)
P(1)–Ni(1)–Ni(2)	88.04(2)	P(1)–C(1)–P(2)	109.4(1)
Ni(1)–Ni(2)–P(2)	97.93(2)	C(5)–P(1)–C(1)	103.7(1)
C(1)–P(2)–Ni(2)	112.04(9)	P(1)–Ni(1)–P(4)	103.10(3)
C(1)–P(1)–Ni(1)	124.7(1)	Ni(1)–C(37)–O(1)	176.0(3)
Ni(1)–Ni(2)–C(37)	147.2(1)	P(1)–Ni(1)–C(37)	106.2(1)
Ni(2)–Ni(1)–C(38)	47.94(9)	P(4)–Ni(1)–C(37)	106.4(1)
Ni(1)–C(38)–Ni(2)	83.3(1)	C(37)–Ni(1)–C(38)	100.6(1)

crystal structure analysis. An ORTEP drawing of the structure is presented in Fig. 1, while a list of important bond distances and angles is given in Table 1.

A detailed examination of these data reveals some interesting information. The Ni–Ni separation (2.5389(5) Å) which is significantly shorter than in the dppm complex (2.694(1) Å) [6] is close to that observed for the analogous complex of the strong π-acceptor ligand $(F_3C)_2P$–S–$P(CF_3)2$ (2.577(5) Å) [7]. The trend of decreasing Ni–Ni separations with increasing π-acceptor properties of the ligands has been discussed [8]. The Ni–C and C–O bond lengths are also notably modified because of the less efficient π-backbonding, as previously noticed in the IR spectrum. The metal–carbon separations are longer (Ni–CO(terminal) in **2**: 1.763(3) and 1.772(3) Å vs. 1.525(9) Å) whereas the C–O separations are shortened (1.148(4) and 1.143(4) Å in **2** vs. 1.299(9) Å). This shortening of the C–O bonds is also apparent on the bridged carbonyl (1.166(3) Å in **2** vs. 1.230(8) Å). Another interesting structural feature is provided by the opening of the P(1)–C(1)–P(2) angle (109.4(1)°) which is closer to that observed for an sp^3 carbon than one could expect (103.9(7)° in the dppm complex). Apparently, the sp^2 hybridization of C(1) does not limit the flexibility of this angle. Although no direct comparison can be drawn, because of the different hybridization of the two types of phosphorus atoms, the phosphinine–Ni separations (2.1448(8) and 2.189(8) Å) are significantly shorter than those of the Ph_2P–Ni bonds (2.2355(8) and 2.2263(8) Å) which are close to those observed in the dppm complex (2.204(1) and 2.203(1) Å) [6]. Otherwise, the structural parameters of the phosphinine ligand are very similar to those found in other nickel(0) complexes [9,10].

2.2. Electrochemical study

In order to evaluate more precisely the resulting effects of the coordination of the phosphinine ligand on the electronic nature of the Ni_2 core, a comparative electrochemical study of the dppm complex and of **2** was undertaken. These experiments were performed in THF (20 °C) containing n-Bu_4NBF_4 (0.3 M) at a stationary gold disk electrode with a scan rate of $0.2\ V\ s^{-1}$. The cyclic voltammograms of the two complexes are presented in Fig. 2. As can be seen, the two curves both display different shapes at positive and negative values of the potential applied. It appears that the behaviour of the two complexes is strongly different upon oxidation. Whereas the first monoelectronic oxidation wave ($n_{O1} = 0.99 \pm 0.05$) of the dppm complex ($E^P_{O1} = +0.25$ V vs. SCE), which can be assigned to the formation of the Ni(I)–Ni(0) species, is reversible (Eq. (3)), the corresponding wave of the phosphinine complex ($E^P_{O'1} = 0.52$ V vs. SCE) remains irreversible even under forcing conditions (scan rate $200\ V\ s^{-1}$) (Eq. (4)).

$$[Ni_2(CO)_3(dppm)_2] \underset{\text{reversible at } O_1}{\overset{-1e^-}{\rightleftharpoons}} [Ni_2(CO)_3(dppm)_2]^+ \quad (3)$$

$$[Ni_2(CO)_3(\mathbf{1})_2] \underset{\text{irreversible at } O'_1}{\overset{-1e^-}{\rightarrow}} [Ni_2(CO)_3(\mathbf{1})_2]^+ \quad (4)$$

This observation is in good agreement with previous conclusions. Firstly, it confirms the low stability of electron deficient phosphinine complexes of Group 10 [11]. Secondly, as expected, the oxidation potential of **2** is shifted anodically with respect to that of the dppm complex, thus confirming that the Ni_2 core is more electron deficient (see discussion about the X-ray structure). Finally, we found that for both complexes, the second oxidation wave which gives the Ni(I)–Ni(I) complex is irreversible ($E^P_{O2} = +0.70$ V vs. SCE, dppm complex; $E^P_{O'2} = +0.90$ V vs. SCE, **2**).

Upon reduction the electrochemical properties of the two complexes also appear to be markedly different. The voltammogram of complex **2** exhibits one partially reversible peak ($E^P_{R'1} = -1.91$ V vs. SCE) which be-

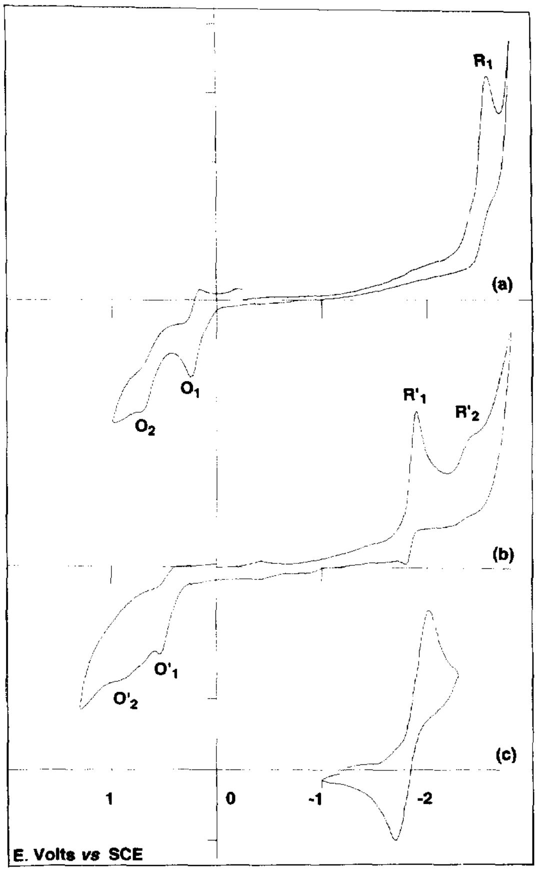


Fig. 2. Cyclic voltammograms of complexes $[Ni_2(CO)_3(dppm)_2]$ and **2** (2 mM in THF, 0.3 M n-Bu_4NBF_4, 20 °C) at a gold disk electrode (diameter 0.5 mm): (a) complex $[Ni_2(CO)_3(dppm)_2]$ ($0.2\ V\ s^{-1}$); (b) complex **2** ($0.2\ V\ s^{-1}$); (c) complex **2** ($5\ V\ s^{-1}$).

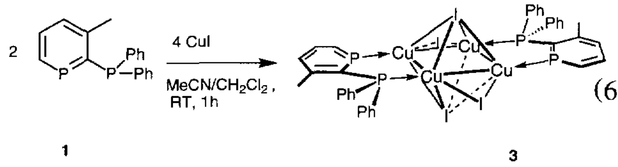
comes totally reversible at 2 V s^{-1} and another one of smaller magnitude ($E^{P}_{R2} = -2.40$ V vs. SCE) which remains irreversible even at high scan rates. Whereas no investigation has been made to assign the nature of this second reduction wave, a determination of the absolute number of electrons ($n_{R'1} = 1.05 \pm 0.05$) shows that the first wave involves a monoelectronic transfer which affords the anion radical complex $[Ni_2(CO)_3(\mathbf{1})]^{\cdot-}$ (Eq. (5)).

$$[Ni_2(CO)_3(\mathbf{1})_2] \underset{\text{reversible at } R'_1}{\overset{+1e^-}{\rightleftharpoons}} [Ni_2(CO)_3(\mathbf{1})_2]^{-\cdot} \qquad (5)$$

On the other hand, the corresponding reduction wave of the dppm complex ($E^{P}_{R1} = -2.60$ V vs. SCE) turns out to be irreversible even under forcing conditions (scan rate 200 V s^{-1}) indicating that the anion radical complex formed is not stable. This comparison underlines once again the good capacity of phosphinine ligands to stabilize electron excessive metallic centres. This behaviour is not unprecedented. A similar statement has been drawn during an electrochemical study of a 2,2′-biphosphinine nickel(0) complex which showed that stable mono- and dianion radical complexes could be electrogenerated upon reduction [10].

2.3. Synthesis and X-ray structure of the $[Cu_4(\mu\text{-}I)_2(\mu_4\text{-}I)_2(\mu\text{-}\mathbf{1})_2]$ complex (3)

The reaction of **1** with 2 equivalents of copper iodide in a mixture of dichloromethane/acetonitrile (5:1) affords complex **3** as a poorly soluble yellow solid which slowly precipitates during the reaction (Eq. (6)). Contrary to complex **2**, the structure of **3** could not be unambiguously deduced from the ^{31}P NMR spectrum which exhibits a sharp AA′XX′ system. Due to its poor solubility in common organic solvents, **3** could not be identified by ^{13}C NMR spectroscopy.



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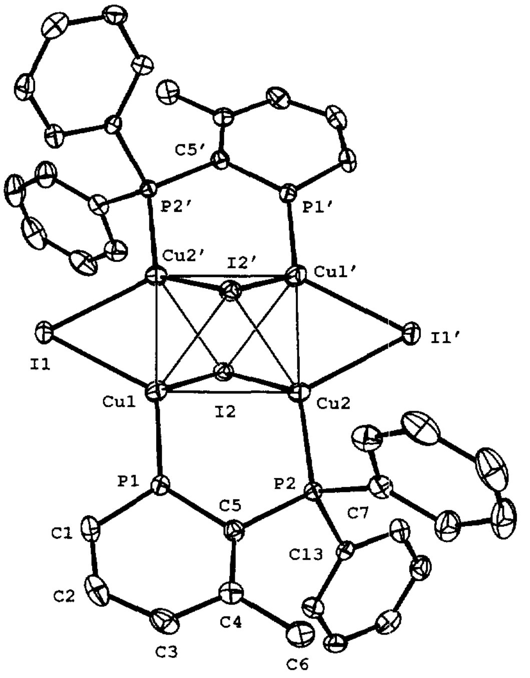
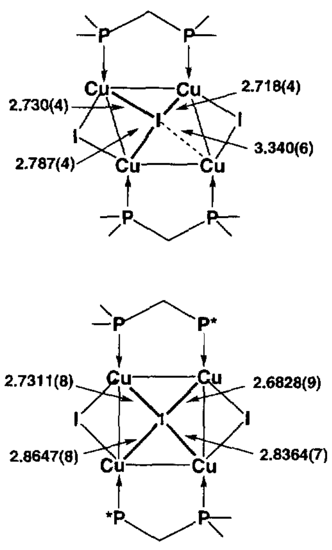


Fig. 3. ORTEP drawing of the molecular structure of complex $[Cu_4(\mu\text{-}I)_2(\mu_4\text{-}I)_2(\mu\text{-}\mathbf{1})_2]$ (**3**) as determined by single crystal X-ray diffraction study with the atomic labelling scheme. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity.

Fortunately, we were able to obtain single crystals of **3** by a slow cooling of a hot chlorobenzene solution. An ORTEP drawing of the structure is presented in Fig. 3, while some bond lengths and angles of interest are given in Table 2. The crystal consists of discrete tetranuclear units $[(CuI)_4(\mathbf{1})_2]$ as expected from the stoichiometry used in the reaction. The structure of **3** may be described as an octahedron having a nearly square planar tetranuclear Cu_4 base (Cu1, Cu1′, Cu2 and Cu2′). Two opposite sides of the Cu_4 square are bridged by two molecules of **1** whereas the two others are asymmetrically bridged by two μ^2-iodide atoms (I1 and I1′ d(Cu(1)–I(1)) = 2.5896(8) and d(Cu(2′)–I(1)) = 2.6370(9) Å). The most surprising feature of this structure concerns the coordination of the two other iodide atoms (I2 and I2′), respectively located at each apex of the octahedron, which display a face μ^4-face-bridging bonding mode. This type of coordination is rare in tetranuclear Cu(I) complexes. μ^4-X (X = Cl, I) binding has been observed in some polynuclear complexes [12] and more recently a similar μ^4-I binding has been described by Puddephatt and coworkers [13] in a te-

Table 2
Selected bond distances (Å) and angles (°) for complex **3**

Cu(1)–Cu(2)	2.848(1)	P(1)–Cu(1)	2.180(1)
Cu(1)–Cu(2′)	2.5516(9)	P(2)–Cu(2)	2.215(1)
Cu(1)–I(1)	2.5896(8)	P(1)–C(1)	1.709(6)
Cu(2′)–I(1)	2.6370(9)	C(1)–C(2)	1.374(8)
Cu(2′)–I(2)	2.7311(8)	C(2)–C(3)	1.394(8)
Cu(1)–I(2)	2.8647(8)	C(3)–C(4)	1.385(9)
Cu(2)–I(2)	2.8364(7)	C(4)–C(5)	1.405(7)
Cu(1′)–I(2)	2.6828(9)	C(5)–P(1)	1.736(5)
Cu(2′)–I(2)	2.7311(8)	C(5)–P(2)	1.831(6)
Cu(2)–Cu(1)–Cu(2′)	90.40(3)	P(1)–Cu(1)–Cu(2)	87.21(5)
Cu(1)–Cu(2)–Cu(1′)	89.60(3)	P(2)–Cu(2)–Cu(1)	95.17(5)
Cu(1)–I(1)–Cu(2′)	58.44(2)	C(5)–P(1)–Cu(1)	104.6(3)
Cu(1)–I(2)–Cu(1′)	86.70(2)	C(5)–P(2)–Cu(2)	116.8(1)
Cu(1)–I(2)–Cu(2)	59.93(2)	P(1)–C(5)–P(2)	111.2(3)
Cu(1)–I(2)–Cu(2′)	54.19(2)	C(1)–P(1)–C(5)	104.6(3)
Cu(1′)–I(2)–Cu(2)	54.99(2)	P(1)–Cu(1)–Cu(2′)	166.79(5)
Cu(1′)–I(2)–Cu(2′)	63.46(2)	P(2)–Cu(2)–Cu(1′)	169.33(5)



Scheme 1. Comparison between the dppm complex and 3. View above the plane supporting the Cu_4 base. P* means P of phosphinine.

tranuclear Cu(I) complex of a phosphonitocavitand. As in this complex, the two μ^4-iodide atoms in complex **3** bind the four copper atoms by means of two short (2.6828(9) and 2.7311(8) Å) and two long (2.8364(7) and 2.8647(8) Å) bond lengths (compare with 2.758(2), 2.752(2), 2.84(2), 2.813(2) Å in the cavitand complex). A direct comparison with the structure of the dppm complex [14] synthesized by Randaccio and coworkers is also of interest. In this case, the two iodide atoms only adopt a μ^3-bridging mode. This difference may be explained by the shortening of the two metal–metal bond lengths, as observed in complex **2**. Indeed, the Cu_4 base in the dppm complex is a parallelogram with two long (3.108(7) Å) and two short (2.682(7) Å) Cu–Cu bond lengths. The deformation of this parallelogram is given by the two openings of the Cu–Cu–Cu angles which appear to be markedly different (101.50 and 78.50°). These data have to be compared with those of complex **3** which exhibit a nearly square planar Cu_4 base (d(Cu–Cu) = 2.848(1) and 2.516(9) Å with 86.90 and 90.40° for the Cu–Cu–Cu angles). Hence, the μ^4 coordination of the two iodide atoms can be simply rationalized in terms of geometry. These atoms are large enough to bridge the Cu_4 edifice which is more compact in **3** than in the dppm complex. A structural comparison between these two structures is presented in Scheme 1. The strong coordination of the phosphinine unit onto the Cu_4 core is also evidenced by the presence of short P–Cu distances (2.180(1) Å) which are the shortest known to date (compare with other phosphinine complexes [15] $2.2090(6) < d < 2.3286(9)$ Å). The P–Cu distances between the PPh_2 groups and the copper atoms (2.215(1) Å) appear to not be modified and are close to those observed in the dppm complex (2.218(8) and 2.230(8) Å). Finally, as we previously noticed in complex **2**, the flexibility of the P–C–P angle in the ligand can also be compared with that of dppm (111.20(3)° in **3** vs. 114.0(1)° in the dppm complex).

3. Experimental details

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry THF, benzene and hexane were obtained by distillation from Na/benzophenone, dry CH_2Cl_2 and acetonitrile were obtained by distillation from P_2O_5. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were obtained on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. The following abreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; b, broad. Elemental analyses were performed by the "Service d'analyse du CNRS", at Gif sur Yvette, France. $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$ [5], $Ni(COD)_2$ [16] and $NiBr_2 \cdot DME$ [17] were prepared according to published procedures.

3.1. Preparation of the complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}1)_2]$ (2)

First procedure using $Ni(COD)_2$ complex as precursor: 2-diphenylphosphino-3-methylphosphinine **1** (0.53 g, 1.8 mmol) and $Ni(COD)_2$ (0.50 g, 1.8 mmol) were weighed in two separate Schlenk flasks in a dry box. The two compounds were then dissolved in dry THF (5 ml) under nitrogen atmosphere and the phosphinine was transfered via a cannula into the $Ni(COD)_2$ solution cooled at −80 °C. The resulting solution turned dark instantaneously. After 2 min of stirring, the solution was slowly warmed to 0 °C and CO was bubbled for 1 h. During this time, the solution was slowly warmed to room temperature. After an additional stirring for 20 min, the volume of the dark red solution obtained was then reduced to dryness and COD was extracted with hexanes (10 ml). The black residue obtained after drying was then dissolved in benzene (10 ml), filtered on Celite under nitrogen and concentrated. Upon concentration, a red solid precipitated out of the solution. This solid was collected by filtration under nitrogen.

Second procedure using $NiBr_2 \cdot DME$ complex as precursor: 2-diphenylphosphino-3-methylphosphinine **1** (0.29 g, 1.00 mmol), $NiBr_2 \cdot DME$ (0.31 g, 1.00 mmol) and zinc powder (0.65 g, 10.0 mmol) were weighed under nitrogen in a Schlenk tube. After the addition of THF (5 ml), the resulting solution was stirred at room temperature for 1 h under a slow steam of CO. Nitrogen was then bubbled into the solution for 30 min. After the evaporation of THF, the same work-up as in the first procedure was observed for the isolation of complex **2**. Yield (%); colour; IR (KBr); analytical and NMR spectroscopic data (^{31}P, ^{1}H, ^{13}C) are as follows.

2. 65; orange–red; 1982 (s), 1966 (s), 1814 (m); Anal. Found: C, 66.20; H, 4.78. $C_{39}H_{32}Ni_2O_3P_4{}^{*}3C_6H_6$ Calc.: C, 66.84; H, 4.92%; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 241.65 (AA′XX′, ^2J(A–X) = 328.33, ^2J(A–X′) = 25.11, ^3J(A–A′) = ^3J(X–X′) = 17.82, $P_{A,A'}$ of C_6H_6P), 29.30 (AA′XX′, $P_{X,X'}$ of PPh_2); ^{1}H NMR (CD_2Cl_2): δ 1.94 (bs, 6H, Me), 7.00–7.70 (m, 4 × C_6H_5 and H_4, H_5 and H_6); $^{13}C\{^1H\}$ NMR: δ 26.40 (s, Me of C_6H_6P), 130.50–131.35 (m, C_6H_5), 132.62 (d, ^1J(C–P) = 11.85, C_2), 134.30 (d, J(C–P) = 14.00, C_4 or C_5), 139.55 (m, C_5 or C_4), 144.50 (m, C_3), 153.40 (m, C_2), 201.10 (m, CO).

3.2. Preparation of the complex $[Cu_4(\mu\text{-}I)_2(\mu_4\text{-}I)_2(\mu\text{-}I)_2]$ (3)

To a solution of 2-diphenylphosphino-3-methylphosphinine **1** (0.29 g, 1 mmol) in a mixture of acetonitrile/dichloromethane (1:5) (60 ml) was added at room temperature copper iodide (0.38 g, 2 mmol). The resulting heterogeneous solution was then stirred at 40 °C for 2 h. During this period, the solution became slowly homogeneous. After filtration under nitrogen atmosphere to remove traces of unreacted CuI, the solvents were evaporated and the resulting yellow powder obtained was successively washed with hexane (3 × 20 ml) and ether (2 × 20 ml) in order to remove traces of unreacted phosphinine. After drying, complex **3** was crystallized in a mixture of dichloromethane/hexane. Yield (%); colour; m.p.; analytical and NMR spectroscopic data (^{31}P, ^{1}H) are as follows.

3. 80; yellow; 140 °C (dec.); Anal. Found: C, 31.95; H, 2.35. $C_{36}H_{32}Cu_4I_4P_4$ Calc.: C, 32.02; H, 2.39%; $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 199.45 (AA′XX′, $^2J(P_A–P_X) + {}^3J(P_A–P_{X'})$ = 248.15, P_A of C_6H_6P), −9.65 (AA′XX′, P_X of PPh_2); ^{1}H NMR ($CDCl_3$): δ 1.82 (m, 6H, Me of C_6H_6P), 7.20–7.60 (m, 22H, 2 × C_6H_6 and H_4 of C_6H_6P), 7.80 (m, 2H, H_5 of C_6H_6P), 8.30 (m, 2H, H_6 of C_6H_6P).

3.3. Electrochemical study of complex 2

Transient cyclic voltammetry was performed in a ca. 12 ml three-electrode airtight cell connected to a Schlenk line. The working electrode consisted of a gold disk of 0.5 or 0.125 mm diameter made from a cross-section of a gold wire (Goodfellow) sealed in glass. The reference electrode was an SCE (Tacussel), separated from the solution by a bridge (3 ml) filled with a 0.3 M solution of n-Bu_4NBF_4 in THF identical to the one used in the cell. The counter electrode was a platinum spiral of ca. 1 cm^2 apparent surface located within 5 mm of the working electrode and facing it. An Electrochemical Digital Analyzer DEA-I (Radiometer Copenhagen) which includes a DEA 332 potentiostat equipped with positive feedback for ohmic drop compensation was used for the experiments. The cyclic voltammetric measurements were performed on 2 mM solutions of the complex. The absolute number of electrons was determined by a combination of chronoamperometry and cyclic voltammetry on a stationary gold disk ultramicroelectrode (0.25 μm), with ferrocene (for the first monoelectronic reduction wave of **2**) and anthracene (for the first oxidation wave of the dppm complex) as reference, according to a published procedure [18].

3.4. X-ray structure determination of $[Ni_2(\mu\text{-}CO)(CO)_2(1)_2]$ (2)

Crystals of **2**, $C_{39}H_{32}Ni_2O_3P_4{}^{*}3C_6H_6$, were grown from a benzene solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf–Nonius MOLEN package. The compound crystallizes in space group *Pbca* (61), $a = 19.535(2)$ Å, $b = 24.488(2)$ Å, $c = 20.879(2)$ Å; $V = 9988.1(2.8)$ Å^3; $Z = 8$; $d_{calc} = 1.362$ g cm^{-3}; $\mu = 9.3$ cm^{-1}; $F(000) = 4256$. A total of 15603 unique reflections were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 7765 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 7838 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.07. The final agreement factors were $R = 0.038$, $R_w = 0.050$, G.O.F. = 1.02.

3.5. X-ray structure determination of $[Cu_4(\mu\text{-}I)_2(\mu_4\text{-}I)_2(1)_2]$ (3)

Crystals of **3**, $C_{36}H_{32}Cu_4I_4P_4$, were grown from a benzene solution of the compound. Data were collected at −150 ± 0.5 °C on an Enraf–Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf–Nonius MOLEN package. The compound crystallizes in space group $P\bar{1}$ (No. 2), $a = 9.124(1)$ Å, $b = 10.359(2)$ Å, $c = 11.385(2)$ Å, $\alpha = 80.97(1)°$, $\beta = 71.84(2)°$, $\gamma = 85.80(1)°$; $V = 1009.50(39)$ Å^3; $Z = 1$; $d_{calc} = 2.221$ g cm^{-3}; $\mu = 53.0$ cm^{-1}; $F(000) = 636$. A total of 6204 unique reflections were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 2302 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 3902 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.05. The final agreement factors were $R = 0.035$, $R_w = 0.042$, G.O.F. = 1.04.

Acknowledgements

The authors thank the CNRS, Ecole Polytechnique and ELF Atochem for financial support of this work.

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