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NEW BIS(DIPHENYLPHOSPHINO)METHANE-BRIDGED $d^{10}-d^{10}$ HETEROBINUCLEAR COMPLEXES DERIVED FROM Ni(CO)₂(η^{1} -Ph₂PCH₂PPh₂)₂ AND Ni₂(μ -CO)(CO)₂(μ -Ph₂PCH₂PPh₂)₂: THE CRYSTAL STRUCTURE OF NiCu(CO)₂(μ -Ph₂PCH₂PPh₂)₂(BH₃CN)

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Abstract—Syntheses of the $d^{10}-d^{10}$ ionic complexes [NiCu(CO)₂(μ -dppm)₂(MeCN)₂]X (dppm = Ph₂PCH₂PPh₂, X = ClO₄, BPh₄ or PF₆), containing four-coordinate copper, and the related complex NiCu(CO)₂(μ -dppm)₂(BH₃CN) from reactions of Ni(CO)₂(η ¹-dppm)₂ with copper(I) species are reported as is the crystal structure of the second of these compounds. This shows a tetrahedral arrangement about nickel(0), a slightly distorted trigonal planar arrangement about copper(I), a Ni—Cu distance [3.171(4) Å] which is too great for significant metal-metal interaction, and a cradle type of arrangement for the Ni—Cu-dppm framework in the solid state. Attempts to prepare related $d^{10}-d^{10}$ Ni(0)—M(I or II) (M = Ag, Au, Zn or Hg) complexes by similar methods were not successful but a Ni—Au complex of limited stability can be identified in related reactions involving Ni₂(μ -CO)(CO)₂(μ -dppm)₂.

Heterobinuclear (and polynuclear) organometallic complexes are of considerable current interest because of their catalytic potential and because of their potential to exhibit quite different reactivities at the two metal sites. Accordingly, several synthetic routes to such systems, both with¹ and without²⁻⁵ metal-metal bonds, have been developed. The stability of the metal-metal framework is enhanced by the presence of a bidentate ligand linking the two metal centres and the ligand chosen is frequently bis(diphenylphosphino)methane (dppm). Probably the most common approach to these dppm-bridged heterobimetallics is the treatment of a mononuclear complex containing mono-coordinated^{1,5-8} or chelate⁹⁻¹³ (where ring strain leads to easy opening of one of the M—P linkages) dppm with a suitable derivative of another metal.

Over the past few years, we have developed and explored the scope of a very simple synthesis of M/CO/phosphine complexes directly, and in one experimental step, from readily available transition metal salts.¹⁴ For the most part, the products obtained have been dppm-bridged homobinuclear cobalt^{15,16} and nickel^{15,17} species or higher nuclearity palladium¹⁸ and platinum¹⁹ systems although, occasionally, heterobinuclear species such as the novel dppm-bridged cobaltaborane CoBH₂(CO)₂ $(\mu$ -dppm) $(\eta^1$ -dppm)²⁰ and CoRh(CO)₃ $(\mu$ -dppm)₂²¹ are obtainable from this one-step procedure. However, mononuclear systems containing mono-coordinated dppm, such as $CoCl(CO)_2(\eta^1-dppm)_2$ (1),⁸ [Co(CO)₂(η^2 -dppm)(η^1 -dppm)]Cl (2)⁸ and $Ni(CO)_2(\eta^1$ -dppm)_2 (3),⁶ are also easily obtainable

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by this route and these are clearly useful starting points for the synthesis of heterobimetallics. Thus, preliminary work with the first of these complexes has shown that dppm-bridged Co-Rh,⁸ Co-Mn¹ and Co-Re¹ carbonyls are readily accessible while reactions of the nickel complex with appropriate platinum⁶ and palladium^{6,7} systems has lead to the formation of the structurally interesting d^{10} - d^8 complexes NiMCl₂(μ -CO)(μ -dppm)₂ (M = Pt, Pd).

In this context, and as part of our ongoing studies¹⁴ of homo- and heteronuclear metal carbonylphosphine complexes, we therefore report here the syntheses and characterizations of some dppmbridged heterobimetallic $d^{10}-d^{10}$ complexes (of which there are few examples in the literature) derived from Ni(CO)₂(η^1 -dppm)₂ and Ni₂(μ -CO)(CO)₂(μ -dppm)₂.

EXPERIMENTAL

Reagents and solvents

Bis(diphenylphosphino)methane (dppm) was obtained from Strem Chemicals, Inc. and was used without further purification. The complexes Ni(CO)₂(η^1 -dppm)₂,⁶ Ni₂(μ -CO)(CO)₂(μ -dppm)₂¹⁷ and [Cu(MeCN)₄]ClO₄²² were prepared by published methods while all other chemicals were reagent grade and were used without further purification. All the solvents used were reagent grade and were degassed prior to use and stored under N₂ in a glove box wherein all work-up procedures were carried out.

Physical measurements

Samples and reagents were protected from atmospheric oxidation during weighing and data collection. Microanalyses for C, H and N were acquired in our laboratories using a Control Equipment Corporation model 240XA analyzer with V₂O₅ being used as a combustion aid. FTIR spectra (Nujol mulls) were recorded on a Bruker IFS 66 spectrophotometer. A Bruker AC-E 200 NMR spectrometer, equipped with a variable temperature controller (BVT-1000S), was used to record ¹H and ${}^{31}P{}^{1}H$ spectra at 200 and 81 MHz, respectively. Chemical shifts are reported as δ values with positive shifts downfield of internal Me₄Si for ¹H spectra and downfield of external 85% H₃PO₄ for ³¹P spectra. For the ³¹P spectra, frequency lock was provided either by a deuterated solvent or, in the cases of reaction mixtures in which deuterated solvents were not used, a coaxial D₂O insert. Mass spectra (EI) were acquired using an Hitachi RMU-7 spectrometer.

Synthesis of $[NiCu(CO)_2(\mu-dppm)_2(MeCN)_2]ClO_4 \cdot 0.4CH_2Cl_2$ (4a)

A solution of Ni(CO)₂(η^1 -dppm)₂(1.0 g, 1.1 mmol) in benzene (20 cm³) was mixed with [Cu(MeCN)₄]ClO₄ (0.4 g, 1.2 mmol) in MeCN (20 cm³) under CO and the mixture was stirred at room temperature for 1 h during which time the solution turned from almost colourless to yellow-green. The mixture was then filtered, hexane (20 cm³) and ethyl ether (20 cm³) were added to the filtrate, and the solution was set aside at 0°C for 3 days after which the crude product was isolated by filtration. Recrystallization from dichloromethane gave the pure product (73% yield) as a yellow-green solvate. Found: C, 58.4; H, 4.5; N, 2.2. Calc. for $C_{56.4}H_{50.8}O_6P_4$ N₂Cl_{1.8}NiCu: C, 58.3; H, 4.4; N, 2.4%. The presence of CH₂Cl₂ was confirmed by mass spectrometry and ¹H NMR spectrometry with the amount present being estimated from the ¹H spectrum. ¹H NMR (CD₃COCD₃): δ 1.9 (s, CH₃CN), 3.1 (m, br, P-CH₂-P), 5.3 (s, CH₂Cl₂). ³¹P NMR (CD₂Cl₂, ambient temp.): AA'XX' pattern δ 22.9 (10 peaks, well resolved, Ni—P), -12.0 (2 broad signals, Cu-P; at $-71^{\circ}C$, these Cu-P signals resolve into an 8 peak system—see discussion). IR (Nujol): v(CO) 2000 (s), 1918 (s); v(ClO₄) 1088 (s, br) cm^{-1} . The non-solvated complex can be isolated in lower yield by treatment of the crude reaction filtrate with hexane only (20 cm³). Found: 59.6; H, 4.6; N, С, 2.2. Calc. for $C_{56}H_{50}O_6P_4N_2ClNiCu: C, 59.6; H, 4.5; N, 2.5\%$.

Synthesis of $[NiCu(CO)_2(\mu-dppm)_2(MeCN)_2]X \cdot CH_2Cl_2 (X = BPh_4, 4b; X = PF_6, 4c)$

These complexes were readily prepared by metathetical reactions in which 4a (1 g, 0.86 mmol) in CH_2Cl_2 (10 cm³) was treated with either NaBPh₄ (0.6 g, 1.8 mmol) in THF (2 cm^3) or solid NaPF₆ (0.3 g, 1.8 mmol) followed by stirring for 2 h. Hexane was then added until the solutions became slightly cloudy at which point ethyl ether was allowed to diffuse slowly into the solutions, yielding yellow-green crystalline deposits. These contained small amounts of unreplaced ClO₄⁻ and final purification was effected by redissolving the crude products in the minimum of CH₂Cl₂ and again adding to the appropriate solution NaBPh₄ (0.6 g) in THF (2 cm^3) or solid NaPF₆ (0.3 g). Addition of hexane followed by ethyl ether diffusion, as outlined above, produced the pure crystalline complexes 4b or 4c. For 4b, Found: C, 68.1; H, 5.0; N, 2.2. Calc. for $C_{81}H_{72}O_2P_4N_2Cl_2BNiCu: C, 67.9; H, 5.1; N,$ 2.0%. ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, ambient temp.): AA'XX' pattern, δ 23.5 (12 peaks, well resolved,

Ni—P), -13.0 (four broad peaks, poorly resolved, Cu—P). IR (Nujol): v(CO) 2000 (s), 1945 (s); v(CN) 2320 (m), 2275 (m) cm⁻¹. For 4c, Found: 4.8; C, 60.1; H, N, 2.3. Calc. for $C_{57}H_{52}O_2P_4N_2Cl_2NiCu: C, 59.8; H, 4.6; N, 2.5\%$ ³¹P{¹H} NMR (CD₂Cl₂, ambient temp.): AA'XX' pattern, δ 23.1 (10 peaks, well resolved, Ni—P), 13.0 (four broad peaks, poorly resolved, Cu-P). IR (Nujol): v(CO) 2020 (s), 1925 (s); v(CN) 2320 (m), 2275 (m) cm⁻¹. The presence of CH_2Cl_2 in both complexes was confirmed by mass spectrometry.

Synthesis of NiCu(CO)₂(μ -dppm)₂(BH₃CN) · CH₂Cl₂ (**5a**)

Method (a). NiCl₂ \cdot 6H₂O (0.5 g, 2.0 mmol) suspended in benzene (20 cm³) and dppm (2.8 g, 7.3 mmol) in ethanol (20 cm³) were mixed and stirred under CO for 30 min. NaBH₃CN (0.5 g, 9.6 mmol) in ethanol (10 cm³) was then added and the resulting mixture was stirred under CO for a further 2 h. The almost colourless solution so obtained was treated with $CuCl_2 \cdot 2H_2O(0.36 \text{ g}, 2.1 \text{ mmol})$ in ethanol (10 cm³), stirring under CO was continued for 1 h, and the resulting yellow-green crude product (66% yield) was collected by filtration. Purification was effected by carrying out the following recrystallization procedure twice. The solid was dissolved in the minimum of CH_2Cl_2 and enough hexane was added to produce the first traces of cloudiness. Ethyl ether was then allowed to diffuse slowly into the solution at room temperature and well-formed yellow-green crystals were obtained. Found: С, 60.6; H, 4.6; N, 1.3. Calc. for C₅₄H₄₉O₂P₄NCl₂BNiCu: C, 60.5; H, 4.6; N, 1.3%. ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, ambient temp.): AA'XX' pattern, δ 23.0 (10 peaks, well-resolved, Ni—P), -17.1 (four broad peaks, poorly resolved, Cu—P). IR (Nujol): v(CO) 2000 (s), 1958 (s); v(BH) 2320; v(CN) 2190 (s) cm⁻¹. The presence of CH₂Cl₂ in the product was confirmed by mass spectrometry.

Method (b). Compound **4a** (0.25 g, 0.22 mmol) was dissolved in toluene/MeCN (2:1, 15 cm³) and CO was passed through the solution for 5 min. NaBH₃CN (0.05 g, 0.80 mmol) suspended in MeCN (5 cm³) was then added in one portion and the resulting yellowish solution was stirred for a further 1 h. A mixture of hexane and ethyl ether (1:1, 30 cm³) was added to precipitate the crude product **2** (86% yield) and the pure complex was isolated by recrystallization from CH₂Cl₂ using the ethyl ether diffusion technique.

Synthesis of [NiAu(CO)₂(µ-dppm)₂]Cl (6)

Under a slow stream of N_2 , a mixture of MeCN and benzene (1 : 1, 40 cm³) was chilled in an ice/salt bath for 15 min. To this chilled solvent mixture, under a stream of CO, were added $Ni_2(\mu$ - $CO(CO)_2(\mu$ -dppm)₂ (0.56 g, 0.58 mmol) and AuCl(SMe₂) (0.26 g, 0.88 mmol). The resulting cold solution was stirred under CO for 45 min during which time it changed colour from orange to bright yellow. After filtration of the reaction mixture, the solvent was removed by evaporation under a stream of CO to give crude 6 as a yellow solid which decomposed during all attempts to recrystallize it from a variety of solvents. ³¹P NMR (reaction mixture after filtration): AA'XX' pattern, δ 35.4 (seven peaks, well resolved), 31.2 (seven peaks, well resolved); the spectrum revealed only traces of other phosphorus-containing products in the reaction mixture. IR (crude solid product, Nujol): v(CO) 2010 (s), 1948 (s) cm⁻¹.

Synthesis of $[Ag_2(\mu-dppm)_3](NO_3)_2 \cdot CH_2Cl_2$ (7)

The complex Ni(CO)₂(η^{1} -dppm)₂ (0.28 g, 0.03 mmol) in toluene (15 cm³) and AgNO₃ (0.055 g, 0.032 mmol) in MeCN (15 cm³) were mixed and stirred at ambient temperature for 1 h during which time an almost colourless precipitate formed. Filtration, followed by washing with toluene, gave the unsolvated complex (0.35 g, 73%) as a white solid and recrystallization of this from CH₂Cl₂ yielded the pure solvated complex 7. Found: C, 58.1; H, 4.8; N, 2.1. Calc. for C₇₆H₆₈O₆P₆N₂Cl₂Ag₂: C, 57.9; H, 4.3; N, 1.8%. The ³¹P NMR shows a complex pattern, centred at δ – 1, arising from the presence of three isotopomers (¹⁰⁷Ag⁻¹⁰⁷Ag⁻¹⁰⁹Ag and ¹⁰⁹Ag⁻¹⁰⁹Ag)—see discussion.

Crystal structure determination of $NiCu(CO)_2(\mu-dppm)_2(BH_3CN) \cdot 0.4CH_2Cl_2$ (5b)

Crystals of **5b** (containing approximately 0.4 molecules of CH_2Cl_2 per molecule of the complex) suitable for X-ray examination were obtained, as flat hexagonal prisms elongated along one axis, by dissolving the crude product obtained from the synthetic procedure outlined above in dichloromethane followed by diffusing dry ethyl ether into the solution. A crystal with dimensions $0.1 \times 0.2 \times 0.6$ mm was chosen for diffraction studies and was mounted on a glass fibre.

Crystal data. $C_{53,4}H_{47,8}O_2P_4NCl_{0,8}BNiCu$, $F_w = 1020.9$, triclinic, $P\bar{1}$, a = 11.411(7), b = 14.937(6), c = 17.045(6) Å, $\alpha = 79.66(4)$, $\beta = 76.34(5)$, $\gamma = 71.27(4)^\circ$, V = 2656(2) Å³, Z = 2, $D_c = 1.276$ g cm⁻³, F(000) = 1053.4, $\lambda = 0.70930$ Å, $\mu(Mo-K_{\alpha}) = 9.53$ cm⁻¹, T = 295 K.

Data collection, structure solution and refinement. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo- K_{α} radiation at 295 K. Unit cell parameters were obtained by least squares analysis of 25 reflections in the range $4^{\circ} \leq 2\theta \leq 27^{\circ}$. Intensity data were corrected for Lorentz-polarization factors; an empirical ψ -scan absorption correction was applied. Three representative reflections were measured every 1.25 h; long-term decay was 12%. The structure was solved using a combination of direct methods and difference Fourier techniques. An ORTEP view of the molecular structure is shown in Fig. 1. Atomic scattering factors were taken from tabulated values.²³ All atoms were refined isotropically except for the phenyl carbons and the solvent atoms. Hydrogen atoms were not included in the model structure. Considerable difficulty was encountered in attempting to refine the solvent, CH₂Cl₂. The final model includes 0.4 molecules of CH₂Cl₂ per formula unit. Chlorine atoms were located in the difference Fourier and positional parameters were refined isotropically. The solvent C atom was located in the difference Fourier but positional parameters could not be refined. The isotropic thermal parameter for all three solvent atoms was set at U = 14.0. No improvement was observed with counterweights so unit weights were used. The final *R* value $[R = \Sigma(||F_o| - |F_c||)/\Sigma F_o]$ was 0.081 for 334

parameters and 3454 observed reflections, $I > 3\sigma(I)$. The final difference Fourier showed four positive peaks, the largest being 1.250 e Å⁻³, near the disordered solvent. The largest negative peak, also near the solvent, was 0.460 e Å⁻³. Selected atomic distances and angles are given in Table 1. Calculations were performed on a 486 PC using a PC version of NRCVAX.²⁴

RESULTS AND DISCUSSION

Treatment of Ni(CO)₂(η^1 -dppm)₂ (3) in benzene with [Cu(MeCN)₄]ClO₄ in acetonitrile, followed by precipitation of the crude product with hexane/ ethyl ether and recrystallization from dichloromethane, afforded a product in good yield which microanalytical and spectroscopic data showed to be the dichloromethane-solvated heterobinuclear complex [NiCu(CO)₂(μ -dppm)₂(MeCN)₂]ClO₄ · 0.4CH₂Cl₂ (4a). The unsolvated complex can be obtained by a slight modification of the isolation procedure (Experimental section) but neither form could be obtained as X-ray quality crystals.

The infrared spectrum of **4a** in the carbonyl region [ν (CO) 2000, 1918 cm⁻¹] is similar to that reported⁶ for **3** [ν (CO) 1992, 1930 cm⁻¹] and the environments about the nickel centres in the two



Fig. 1. The molecular structure of NiCu(CO)₂(μ -dppm)₂(BH₃CN) \cdot 0.4CH₂Cl₂ (5b).

New bis(diphenylphosphino)methane-bridged d^{10} - d^{10} heterobinuclear complexes

Table	1.	Selected	bond	distances	(Å)	and	angles	(°)	for	NiCu(CO) ₂ (µ-
$dppm)_2(BH_3CN) \cdot 0.4CH_2Cl_2$ (5b)										

Ni—Cu	3.171(4) ^a	Cu—P3	2.239(5)
Ni—C1	1.78(2)	Cu—N	1.96(2)
NiC2	1.76(2)	NC3	1.14(2)
NiP2	2.207(5)	С3—В	1.59(3)
NiP4	2.216(5)	P1—P2	3.028(6) ^a
C1—O1	1.14(2)	P3—P4	3.047(6) ^a
C2—O2	1.14(3)	Cu—C1	$2.74(2)^{a}$
Cu—P1	2.247(5)	Cu-Ol	$3.26(2)^{a}$
P2NiP4	109.5(2)	Ni-C2-O2	178.0(2)
P2NiC1	115.7(6)	P1—Cu—P3	117.7(2)
P2—Ni—C2	102.7(6)	P1-Cu-N	116.3(5)
P4—Ni—C1	118.2(6)	P3—Cu—N	116.3(5)
P4—Ni—C2	102.8(6)	CuNC3	173.9(2)
C1NiC2	105.7(8)	NC3B	179.1(2)
Ni—C1—O1	166.8(2)		

^aNon-bonded.

complexes are therefore probably much the same. The infrared spectrum also confirms the presence of coordinated acetonitrile [v(CN) 2318, 2275 cm⁻¹] (as does the ¹H NMR spectrum which shows a CH₃ singlet at δ 1.94) and of ionic²⁵ ClO₄⁻ (1088 cm^{-1}). The presence and the amount of solvating dichloromethane are evident from the ¹H NMR spectrum (singlet at δ 5.31). The room-temperature ³¹P NMR spectrum shows a complex AA'XX' pattern of the type which would be expected from a system containing the NiCu(μ -dppm)₂ core. Thus, the A portion of the spectrum is well-resolved (10) peaks) and centred on δ 22.9 while the X portion is poorly-resolved (two very broad signals) and centred on δ -12.0. At -71°C, the X portion of the spectrum resolves into eight well-defined peaks and this confirms that the signals centred on $\delta - 12.0$ are due to the phosphorus atoms coordinated to the copper since these temperature-dependent effects are typical of phosphorus atoms attached to a quadrupolar nucleus such as ⁶³Cu.

The sum of the microanalytical and spectroscopic evidence therefore indicates that **4a** is structurally similar in several respects to the known³ d^{10} - d^{10} Ni—Au system [NiAu(CNMe)₂(μ -dppm)₂]Cl except that in **4a** both metal centres are four-coordinate. Thus, the cation of this most probably has the structure of **4**.

The corresponding BPh_4^- and PF_6^- salts (4b and 4c, respectively) are readily prepared in high yield by metathetical reactions of 4a with an excess of either NaBPh₄ or NaPF₆ in dichloromethane. The spectroscopic properties of these complexes are virtually identical to those of 4a except that for 4b and 4c, the Cu—P portion of the ³¹P spectra are somewhat better resolved (four peaks) at room temperature.

The related complex $NiCu(CO)_2(\mu$ -dppm)₂ $(BH_3CN) \cdot CH_2Cl_2$ (5a) can be prepared in good yield by two methods. The more straightforward procedure is a convenient "one-pot" reaction in which 3 is generated in situ by reducing NiCl₂ \cdot 6H₂O under CO with NaBH₃CN in the presence of dppm. Without isolating 3, this reaction mixture is treated with $CuCl_2 \cdot 2H_2O$ to give 5. Slow diffusion of diethyl ether into a saturated solution of the crude product in CH₂Cl₂/hexane gives the pure solvated complex 5a. The second synthetic approach is the treatment of 4a with NaBH₃CN. The IR spectrum in the carbonyl region is very similar [v(CO) 2000](s), 1958 (s) cm^{-1}] to the spectra of 3 and 4a-4c and this IR spectrum also shows the presence of coordinated BH₃CN [v(BH), 2320 (s); v(CN) 2190 (s) cm⁻¹]. The ³¹P NMR spectrum is superficially similar to those of 4a-4c in that it shows an AA'XX' pattern with the A and X portions at δ 23.0 (10



peaks) and -17.1 (four broad peaks), respectively. The significant difference from the spectra of the ionic complexes **4a-4c** is that the Cu—*P* signal is about 5 ppm further upfield which supports the IR evidence that the BH₃CN group is coordinated to the copper centre. The spectroscopic evidence strongly suggests then that the structure of the complex is as shown in **5**.

That this is correct is shown by an X-ray crystal structure determination of a partially-solvated form $(0.4 \text{ mol } CH_2Cl_2)$ of the complex (5b) obtained by a modified and slower recrystallization process in which no hexane was added prior to the diffusion of ether into the CH₂Cl₂ solution (Experimental section). The molecular structure of this complex is shown in Fig. 1 and selected atomic distances and angles are listed in Table 1. The two dppm ligands bind the two metal centres together in a cradle type of arrangement but the Ni-Cu distance of 3.171(4) Å is too large for any significant metal-metal interaction. The two bridging phosphorus atom "bite" distances are 3.028(6) and 3.047(6) Å, respectively, which are slightly less than the metal-metal distance. The coordination geometry around nickel is tetrahedral with angles of $102.7(6)-118.2(6)^{\circ}$ while the environment around copper is a slightly distorted trigonal planar geometry in which the copper atom is displaced by 0.380(8) Å from the plane of the copper-bonded atoms nitrogen, Pl and P3 towards the nickel atom. The interior angles for this distorted planar arrangement are $116.3(5)^{\circ}$, $116.8(5)^{\circ}$ and $117.7(2)^{\circ}$. The carbon atom Cl, at a distance of 2.74(2) Å from copper, does not bridge the two metal centres.

Since the syntheses described above are very straightforward, an attempt was made to synthesize analogous Ni-Au systems by similar methods. However, no identifiable Ni-Au system could be obtained from reactions, even at low temperatures, of Ni(CO)₂(η^1 -dppm)₂ with AuCl(SMe₂) or Au (CO)₂Cl; the only characterizable product being the known¹⁷ homobinuclear complex $Ni_2(\mu$ -CO)(CO)₂(μ -dppm)₂. Clearly the NiAu(μ -dppm)₂ framework is a stable entity under some conditions since $[NiAu(CNMe)_2(\mu-dppm)_2]Cl$ has been synthesized and characterized crystallographically³ and an alternative approach to the Ni/Au/ dppm/CO system was therefore explored. The route chosen was very similar to the transmetallation procedure used³ for the synthesis of $[NiAu(CNMe)_2(\mu$ dppm)₂]Cl. Thus, Ni₂(μ -CO)(CO)₂(μ -dppm)₂ was treated with AuCl(SMe₂) in acetonitrile/benzene at various temperatures. At room temperature, no Ni-Au complex was characterizable but at lower temperatures (ice-salt bath), such a product was clearly formed although the instability of this prod-

uct was such that a complete characterization could not be carried out. A ³¹P NMR spectrum of the reaction mixture, recorded immediately after the reaction was complete, showed the AA'XX' pattern which would be expected of the NiAu(μ -dppm)₂ core with the A and X portions of the spectrum centred at δ 35.4 (seven peaks, well resolved) and 31.2 (seven peaks, well resolved), respectively. A similar pattern is exhibited³ by $[NiAu(CNMe)_2(\mu$ dppm)₂]Cl. This spectrum showed also that only very small amounts of other phosphorus-containing products were present and the reaction is therefore a high-yield process. Attempts at obtaining a crystalline product from the reaction mixture using the usual isolation techniques led only to decomposition of the complex. However, complete removal of the solvent mixture under a stream of CO gave a pale yellow solid which could not be recrystallized (decomposition) but for which the IR spectrum showed the expected pattern in the carbonyl region [v(CO) 2010 (s), 1948 (s) cm⁻¹]. This pattern is very similar to those observed for 3, 4a-4c and 5a (see earlier discussion). Given the ionic nature³ of [NiAu(CNMe)₂(µ-dppm)₂]Cl, a reasonable formulation for this product would be $[NiAu(CO)_2(\mu-dppm)_2]Cl$ (6) but why this Ni—Au framework is so much more stable when methyl isonitrile rather than CO is bound to the nickel centre is not clear.

Reactions of 3 with other d^{10} systems [Ag(I), Zn(II), Hg(II)] were attempted but no clear evidence for the formation of heterobinuclear systems with any of these metal ions was obtained. Only with Ag(I) was an easily isolable and characterizable product formed. Thus, treatment of 3 with $AgNO_3$ (or Ph₃P or diphos complexes thereof), gave $[Ag_2(\mu-dppm)_3](NO_3)_2 \cdot CH_2Cl_2$ (7) as the only product. A much simpler synthesis of the $[Ag_2(\mu$ $dppm_{3}]^{2+}$ system, in which $AgAsF_{6}^{26}$ or $Ag(O_{3})$ SCF_3 ²⁷ is treated with dppm in a 2:3 ratio, has been reported by others and the synthetic route starting with 3 is therefore of little value. However, 7 does show some interesting ³¹P NMR characteristics as compared with the those of the $AsF_6^$ and $(O_3SCF_3)^-$ salts. Generally speaking, all three systems show much the same kind of ³¹P spectra in that each of these spectra consists of a complex pattern of superimposed signals arising from the presence of the three possible isotopomers (¹⁰⁷Ag-¹⁰⁷Ag, ¹⁰⁹Ag-¹⁰⁹Ag and ¹⁰⁷Ag-¹⁰⁹Ag). The pattern observed for 7 is centred on $\delta - 1$ in CD₂Cl₂ solution. Where the three complexes differ in their behaviour is in how the spectra change with temperature. Thus, at room temperature, the $AsF_6^$ salt exhibits²⁶ a partially resolved spectrum [two greatly broadened singlets flanking a hump centred

on δ 5.9 (acetone)] while the (O₃SCF₃)⁻ salt shows²⁷ only a very broad hump centred on $\delta - 2.7$ (solvent unspecified). At low temperatures $(-60^{\circ}C \text{ and }$ -50° C, respectively), these spectra are fully resolved with the multiplicities and peak areas in the observed and simulated spectra virtually identical in both cases. The spectrum of 7 is, however, almost completely resolved at room temperature and only slight sharpening of the various resonances is observed even at -71° C. The temperature dependence of these spectra has been explained^{26,27} in terms of an intramolecular "endover-end" exchange of the dppm ligands and it appears, therefore, that this exchange is much slower for 7 than for the other two salts. While the exchange rate is undoubtedly dependent to some extent upon the nature of the solvent, it appears that the nature of the anion is also a factor with the rate of exchange in $[Ag_2(\mu-dppm)_3]X_2$ lowest where $X = NO_3$ and highest when $X = O_3SCF_3$.

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