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# Synthesis of bis(diphenylphosphino) ethanenickel(II) organodichalcogenide complexes and cyclotrimerisation reaction of dimethylacetylenedicarboxylate : structure of Ni(dppe)( $SC_6H_4O$ )

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Abstract—Reaction of Ni(dppc)Cl<sub>2</sub> (dppc = bis(diphenylphosphino)ethane) with organodichalcogenide ligands of the type 1,2-HSC<sub>6</sub>H<sub>4</sub>EH (E = CO<sub>2</sub>, O, NH) in the presence of triethylamine to give the products Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>) (1), Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>O) (2), and Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>NH) (3). Complex 2 was characterised by single crystal X-ray diffraction, which shows a distorted geometry. Complexes 1–3 and the dithiolato analogues of 1,2-benzenedithiol, Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>S) (4), and 3,4-toluendithiol, Ni(dppe)(SC<sub>6</sub>H<sub>3</sub>MeS) (5), upon reflux with dimethylacetylenedicarboxylate (DMAD) formed the cyclotrimeric product hexamethylbenzene hexacarboxylate (HMBC). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: nickel(II) complexes; crystal structure; cyclotrimerisation; hexamethylbenzene hexacarboxylate.

Since the discovery of the cyclotetramerisation of acetylene by Reppe [1], a number of transition metal complexes have been found to homogeneously catalyse the cyclisation of acetylenes. Much of this work has centred around the group 10 metals, with the cheaper nickel playing quite a prominent role in these studies. Two oxidation states are predominant in the use of nickel as a catalyst for acetylene cyclisation. These are Ni(II) and Ni(0). Early literature reports considered Ni(II) complexes as the active catalysts in the formation of cyclooctatetraenes [2], whereas Ni(0) complexes trimerise acetylenes to benzenoid derivatives [3,4]. In general, studies involving Ni(0) are more abundant than those of Ni(II) mainly because the former readily dissolve in organic solvents whilst Ni(II) salts, that are normally used, are insoluble in such solvents. With the aid of phosphine ancillary ligands the solubility of Ni(II) complexes in organic

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solvents could be achieved. Such compounds are known to trimerise acetylenes [5]. Recently, Bennet and Wenger [6] have utilised bis(phosphino)nickel(0) complexes to catalytically cyclise a number of alkynes in solution, demonstrating the importance of phosphines in these reactions.

With dithiolato as coligands, phosphinonickel complexes can behave as nucleophilic agents towards acetylenes. Dimethylacetylenedicarboxylate reacts (triphos)Ni( $\eta^2$ -S<sub>2</sub>CS) with (triphos = 1, 1, 1-tris-(diphenylphosphinomethyl)ethane) to form a heterocyclic five-membered metallo-ring adduct, in which a dimerised DMAD moiety is attached to the C and S ends of the  $\eta^2$ -S<sub>2</sub>CS ligand [7]. Adduct formation, through the attachment of dienes to sulfur atoms of bis(1,2-ethylenedithiolato)Ni [8] and of quadricyclane to one sulfur atom of  $(\eta^5-C_5H_5)(1,2-BDT)Co(III)$ (1,2-BDT = 1,2-benzenedithiolato) [9], are known. In an effort to investigate the nucleophilic properties of bis(diphenylphosphino)ethanenickel(II) organodichalcogenide complexes, we reacted the three compounds synthesised in this paper as well as  $Ni(dppe)(SC_6H_4S)$  (4) and  $Ni(dppe)(SC_6H_3MeS)$  (5), the synthesis of which has been reported elsewhere

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[10], with DMAD. Our investigations showed that DMAD readily trimerises to HMBC.

# **RESULTS AND DISCUSSION**

Syntheses of mixed aryldichalcogenide complexes (1-3) were performed in good yields, by adding the appropriate chalcogen containing ligand to a solution of Ni(dppe)Cl<sub>2</sub> and excess Et<sub>3</sub>N (eqn (1)).

 $Ni(dppe)Cl_2 + 1,2-HSC_6H_4EH$ 

$$2Et_{1}N \longrightarrow Ni(dppe)(SC_{6}H_{4}E)$$
  
+ 2Et\_{1}NHCl(E = CO<sub>2</sub> (1), O (2), NH (3)) (1)

All reactions were complete within 2 h and products could be isolated in analytically pure form. The <sup>1</sup>H NMR of complexes 1-3 displays a pattern which is consistent with the different environment of all four protons of the phenyl group of the chalcogen containing ligands. Compound 3 has an additional broad peak at 4.35 pm, corresponding to the NH group of the aminothiophenolate ligand. The non-equivalence of the two phosphorus atoms of the dppe is clearly indicated by different electronic properties between the S and E of the thiolate ligands. This results in a set of multiplets for the ethane moiety in the dppe. For 1 and 3 there are two sets of multiplets, with each set associated with one P atom; but the multiplets for 2 are not well resolved. The  $^{31}P\{^1H\}$  spectra show doublets corresponding to the expected AX (1, 2) or AB (3) spin system. The latter is similar to the peaks pattern for [Ni(dippe)(SR)(CNBu<sup>t</sup>)]<sup>+</sup> (dippe = 1,2bis(diisopropylphosphino)ethane,  $R = C_6 F_5$ ,  $C_6 F_4 H_1$ ,  $C_6H_4F$ , Ph) [11].

Compounds 1–5 are stable indefinitely in the solid state in air at room temperature; but on exposure to air, blue solutions of 3 gradually turn purple in 2 days at room temperature. This is accompanied by the disappearance of the NH peak in the <sup>1</sup>H NMR spectrum. Other phenyl peaks of the aminothiophenolate ligand lose their fine structure gradually and broaden over a period of 12 days.

# Structure of Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>O)

The co-ordination around the nickel is a distorted square-planar, with a maximum deviation from the least-square of NiOSP<sub>2</sub> being 0.19 Å. This deviation from planarity is more pronounced than that found for 4 [10]. The molecular structure of 2 is shown in Fig. 1 and selected bond distances and angles are given in Table 1 and atomic co-ordinates in Table 2. Apart from the Ni—O and the C(1)—O bonds in 2 which do not exist in 4 [10], all other bond distances and angles in the two compounds are comparable. The bond lengths and angles are in the expected ranges for Ni—S [12] and Ni—P [13] distances. In particular the Ni—S and Ni—O distances are similar to those found



Fig. 1. ORTEP drawing of Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>O).

in ["BuNH]<sub>2</sub>[Ni(SC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>], which are 2.153(2) Å and 1.875(3) Å respectively [14].

# Reactions with DMAD

When solutions of compounds 2–5 and DMAD in toluene/CH<sub>2</sub>Cl<sub>2</sub> (1:1) were refluxed, typically for 48 h, HMBC could be isolated (eqn (2)). The reaction is very slow at room temperature and could take up to 1 week to complete, but it is much faster at elevated temperatures.

Ni(dppe)(SC<sub>6</sub>H<sub>3</sub>RE) + R'C 
$$\equiv$$
 CR'  
(R = H (1-4), Me (5); R' = CO<sub>2</sub>Me)  $\xrightarrow{R'}$  R'  
(2)

The product was identified as HMBC by its melting point, IR, <sup>1</sup>H, <sup>13</sup>C NMR and mass spectroscopy (see Experimental section). The efficiency of these complexes to effect the cyclotrimerisation ranges from 4%for 3 to 42% for 5; with the ratio of DMAD to the nickel complexes being about 48:1. Nevertheless the yields for all are better than expected from a stoichiometric reaction except for 3; implying some catalytic activity.

However under similar conditions and work-up procedure, HMBC could not be isolated when 1 reacted with DMAD. A brown precipitate was obtained when solutions, after reflux, were allowed to stand at room temperature for several days. The dominant peak in the <sup>1</sup>H NMR spectrum of this brown solid is 3.88 ppm, with some weak and broad peaks in the phenyl region. <sup>13</sup>C NMR spectrum gave

Ni-S(1)	2.158(10)	Ni—O(1)	1.879(3)	
Ni - P(1)	2.126(1)	Ni - P(2)	2.174(1)	
P(1)—C(8)	1.849(5)	P(2)C(7)	1.830(4)	
P(1)—C(11)	1.815(4)	P(1)C(21)	1.799(4)	
P(2)C(31)	1.816(4)	P(2)C(41)	1.808(4)	
C(7)—C(8)	1.518(7)	S(1)C(6)	1.765(4)	
O(1)—C(1)	1.320(5)	C(1)C(6)	1.389(5)	
O(1)—Ni—S(1)	90.53(9)	O(1)N	√iP(1)	91.85(9)
P(2)— $Ni$ — $P(1)$	86.71(4)	P(2)N	i <b>—</b> S(1)	92.63(4)
O(1)—Ni—P(1)	169.51(10)	S(1)N	iP(1)	170.21(5)
C(6)—S(1)—Ni	95.30(13)	C(1)C	(1)—Ni	115.9(2)
C(7)—P(2)—Ni	108.8(2)	C(8)C	(7) - P(2)	107.0(3)
C(7)—C(8)—P(	l) 107.6(3)	C(8)C	2(7) - P(2)	107.0(3)
O(1)C(1)C(	6) 121.2(3)	C(1)C	S(6) - S(1)	115.6(3)

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

peaks assignable to HMBC as the only significant peaks. The parent peak in EIMS of the solid is m/z = 395 and a molecular peak at m/z = 427 (5.7%), which were also observed as the parent and molecular peaks for HMBC. The 395 peak corresponds to a loss of OMe from HMBC. Other peaks in the spectrum were m/z 683, 825, and 967; which we have not been able to assign to any definitive molecular formula. But the difference between peaks show loss of DMAD (m/z = 142). Based on this data it is evident that 1 also cyclotrimerises DMAD, but the HMBC formed could be adsorbed by some reminant nickel complex, thus making it difficult to separate by column chromatography.

NMR tube reaction of 5 and DMAD allowed the progress of the trimerisation to be monitored by <sup>1</sup>H NMR spectroscopy. There were not significant changes in the spectrum of 5 during the first 30 min. After 4 h new peaks appeared at 7.08 (d), 7.33 and 7.67, all were weak in intensities, in addition to 7.26 (d), 7.21 (s) and 6.63 (m) for 5. Peaks of 5 were significantly weaker after 24 h, and the 7.08 peak observed after 24 h had become quite broad. A distinct HMBC peak at 3.88 had begun to emerge at this stage in the reaction. When the spectrum of the mixture was run after 3 days, the peaks found were the same as those of 24 h but better resolved. The <sup>31</sup>P NMR after 24 h gave two peaks at 58.62 and 48.22 (intensity ratio 2:1); the 58.62 peak is assignable to 5 but the latter is new. However after 7 days of reaction the peak intensities were equal. Finally, <sup>13</sup>C spectrum of this mixture showed the following chemical shifts: 165.2, 152.2, 133.9, 74.5 and 43.4; three of which are the peaks of HMBC (165.8, 133.9 and 53.5). When phenylacetylene and diphenylacetylene were used in place of DMAD, no reaction was observed and the acetylenes could be recovered in near quantitative amounts. This clearly implies that the bulkier and less electrophilic alkynes, could not be activated by the nickel complexes. These observations suggest that the trimerisation process might involve attack of the nickel complex by the alkyne as proposed by Tyler *et al.* [16]. The least efficient of the five complexes in effecting trimerisation was found to be **3** which could be explained by the gradual decomposition of the complex in solution (*vide supra*).

# CONCLUSION

With bidentate phosphines as ancillary ligand, homo and mixed aryldichalcogenide nickel(II) complexes could convert the electrophilic acetylene, DMAD, to HMBC catalytically. However bulky acetylenes are unreactive, most likely due to their inability to be activated by the catalysts. The lack of reactivity by the bulkier acetylenes might mean that the initial step in the cyclisation of DMAD is coordination of the acetylene.

#### EXPERIMENTAL

#### Materials and instrumentation

All solvents were of analytical grade and were used without further purification. The thiols and 1,2-bis(diphenylphosphino)ethane were purchased from Aldrich and were used as received. Ni(dppe)Cl<sub>2</sub> [16], Ni(dppe)(1,2-BDT) (4) and Ni(dppe)(TDT) (5) (TDT = 3,4-toluenedithiolato), were prepared by the literature procedure [10].

IR spectra were recorded on a Mattson Polaris or a Nicolet 205 FT-IR. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR were recorded on a Varian Gemini 2000 or a Gemini 300 and referenced to residual CHCl<sub>3</sub> for <sup>1</sup>H (7.26), <sup>13</sup>C (77.0) and externally to 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. Mass spectra data were collected on a Finnigan MAT SSQ 700 in the electron impact mode and elemental analyses were performed by the microanalytical laboratory

Table 2. Atomic co-ordinates ( $\times$ 10<sup>4</sup>) and equivalent isotropic displacement parameters ( $\dot{A}^2 \times 10^3$ )

	Х	J,	2	$U(eq)^a$
Ni(1)	3400(1)	1189(1)	3633(1)	42(1)
S(1)	4160(1)	2096(1)	3172(1)	50(1)
P(1)	2383(1)	384(1)	4064(1)	46(1)
O(1)	3876(2)	1853(2)	4131(1)	59(1)
C(1)	4583(3)	2473(2)	4040(1)	47(1)
P(2)	3074(1)	267(1)	3109(1)	43(1)
C(2)	5072(4)	2925(3)	4397(2)	61(1)
C(3)	5870(4)	3544(3)	4311(2)	73(1)
C(4)	6130(4)	3746(4)	3864(2)	80(2)
C(5)	5631(4)	3319(3)	3509(2)	67(1)
C(6)	4857(3)	2680(3)	3596(1)	46(1)
C(7)	1842(3)	-321(3)	3246(2)	57(1)
C(8)	1913(4)	- 586(3)	3741(2)	60(1)
C(11)	1181(3)	998(3)	4197(1)	47(1)
C(12)	1074(4)	1871(3)	4049(2)	65(1)
C(13)	146(5)	2328(4)	4140(2)	83(2)
C(14)	-692(4)	1925(4)	4364(2)	78(2)
C(15)	- 586(4)	1074(4)	4505(2)	74(1)
C(16)	344(4)	610(4)	4425(2)	62(1)
C(21)	2877(3)	-26(3)	4596(1)	55(1)
C(22)	2977(3)	- 928(4)	4695(2)	55(1)
C(23)	3387(6)	-1211(5)	5103(3)	104(2)
C(24)	3763(5)	-600(7)	5414(3)	112(3)
C(25)	3664(6)	286(6)	5330(2)	105(2)
C(26)	3232(6)	568(5)	4921(2)	87(2)
C(31)	4112(3)	- 567(3)	3236(2)	49(1)
C(32)	5113(4)	- 346(3)	3097(1)	70(1)
C(33)	5966(5)	-934(4)	3187(3)	95(2)
C(34)	5778(5)	-1745(4)	3007(2)	88(2)
C(35)	4793(6)	-1987(4)	2878(2)	88(2)
C(36)	3940(5)	- 1470(3)	2921(2)	69(1)
C(41)	2956(3)	633(2)	2528(1)	45(1)
C(42)	2076(4)	1096(3)	2389(2)	69(1)
C(43)	1990(5)	1392(4)	1946(2)	87(2)
C(44)	2776(5)	1252(3)	1638(2)	75(1)
C(45)	3665(5)	804(4)	1773(2)	74(1)
C(46)	3769(4)	496(3)	2214(2)	61(1)

"  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

at the University of Cape Town, South Africa, as a service.

#### Syntheses of Ni(dppe)organodichalcogenide complexes

All three complexes were prepared and worked-up in a similar manner and typical procedure is described for Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>CO<sub>5</sub>).

Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>) (1). A mixture of Ni(dppe)Cl<sub>2</sub> (1.0 g, 1.89 mmol) and thiosalicylic acid (0.29 g, 1.89 mmol) was degassed and nitrogen saturated CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) added. To the resultant solution was added Et<sub>3</sub>N (1.00 cm<sup>3</sup>), changing the orange solution to dark red. After stirring the solution for 2 h, hexane (50 cm<sup>3</sup>) was added to give an orange brown precipitate. The solid was washed with copious amount of water and recrystallised from CH2Cl2/hexane. Yield = 0.88 g, 76%, m.p. = 258-260°C. Anal. Calc. for C<sub>33</sub>H<sub>28</sub>O<sub>2</sub>P<sub>2</sub>SNi: C, 65.05; H, 4.63; S, 5.26. Found: C, 63.93; H, 4.70; S, 4.70%. 'H NMR (CDCl<sub>3</sub>): 8.11 (q, 1H), 7.30 (q, 1H), 7.01 (m, 2H) (SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>); 8.03 (m, 8H), 7.51 (m, 12H) (dppe), 2.38 (m, 2H), 2.10 (m, 2H) (dppe).  ${}^{13}C{\{^{1}H\}}$  NMR : 168.9 (s) (SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>), 142.4 (s), 133.5 (d,  $J_{CP} = 10.20$ Hz), 133.1 (d,  $J_{CP} = 10.30$  Hz), 129.2 (d,  $J_{CP} = 8.30$ Hz), 128.7 (s), 123.1 (s) (dppe), 131.9 (s), 131.4 (s), 128.4 (s), 127.4 (s), 126.8 (s) (SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>), 29.7 (d,  $J_{\rm CP} = 15.0$  Hz), 21.9 (d,  $J_{\rm CP} = 15.0$  Hz) (dppe).  ${}^{31}P_1^{(1}H_1^3 \text{ NMR}: 57.19 \text{ (d, } J_{PP} = 59.82 \text{ Hz}\text{), } 41.72 \text{ (d,}$  $J_{\rm PP} = 59.82$  Hz). IR (KBr pellet, cm<sup>-1</sup>): 3043 w, 1592 vs, 1575 vs, 1543 m, 1433 s, 1348 s, 1100 s, 821 s, 752 s, 703 s, 689 s, 528 vs, 488 m.

Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>O) (2). Yield = 0.76 g, 69%; m.p. =  $294-296^{\circ}$ C. Anal. Calc. for  $C_{32}H_{28}OP_2SNi$ : C, 66.12; H, 4.86; S, 5.52. Found: C, 65.56; H, 4.83; S, 4.96%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.08 (t,  $J_{HH} = 9.0$  Hz, 4H), 7.88 (t,  $J_{\rm HH} = 9.0$  Hz, 4H), 7.46 (m, 12H) (dppe), 7.30 (d,  $J_{\rm HH} = 7.41$  Hz, 1H), 6.82 (t,  $J_{\rm HH} = 8.19$  Hz, 1H), 6.72 (d,  $J_{HH} = 7.98$  Hz), 6.50 (t,  $J_{HH} = 7.41$  Hz)  $(SC_6H_4O)$ , 2.60 (m, 4H) (dppe),  ${}^{13}C{}^{1}H$  NMR : 133.3 (dd,  $J_{CP} = 9.3$  Hz), 131.2 (d,  $J_{CP} = 22.6$  Hz), 128.9 (t,  $J_{\rm CP} = 10.3$  Hz) 115.3 (d,  $J_{\rm CP} = 33.2$  Hz) (dppe), 130.9 (s), 130.3 (s), 129.7 (s), 127.6 (s), 122.5 (s)  $(SC_6H_4O)$ , 29.5 (d,  $J_{CP} = 16.0$  Hz), 22.7 (d,  $J_{CP} = 16.0$  Hz) (dppe). <sup>31</sup>P{<sup>1</sup>H} NMR : 58.88 (d,  $J_{PP} = 55.46$  Hz, 1P), 44.97 (d,  $J_{PP} = 55.46$  Hz, 1P). IR (KBr pellet, cm<sup>-1</sup>): 3029 m, 1560 m, 1482 w, 1454 vs, 1434 vs, 1274 s, 1231 m, 1100 s, 1021 w, 871 w, 843 w, 818 w, 743 s, 718 m, 689 vs, 529 vs, 488 m.

Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>NH) (3). Yield = 0.82 g, 75%; decompositon =  $249.1^{\circ}$ C. Anal. Calc. for  $C_{32}H_{29}NP_2SNi: C, 66.23; H, 5.04; N, 2.41; S, 5.53.$ Found : C, 65.31 ; H, 5.03 ; N, 1.94 ; S, 5.23. <sup>1</sup>H NMR  $(CDCl_3)$ : 7.85 (t,  $J_{HH} = 7.80$  Hz, 8H), 7.46 (m, 12H) (dppe), 6.71 (t,  $J_{\rm HH} = 6.80$  Hz, 1H), 6.43 (dd,  $J_{\rm HH} = 13.00, 7.20$  Hz 2H), 4.38 (s, br, 1H)  $(SC_6H_4NH)$ , 2.32 (d, 17.60 Hz, 4H) (dppe). <sup>13</sup>C{<sup>1</sup>H} NMR : 133.5 (d,  $J_{CP} = 11.1$  Hz), 131.3 (d,  $J_{CP} = 17.6$ Hz), 129.2 (d,  $J_{CP} = 9.9$  Hz), 128.7 (d,  $J_{CP} = 10.3$  Hz) (dppe), 130.0 (s), 127.6 (s), 121.8 (s), 112.9.5 (s)  $(SC_6H_4NH)$ , 27.9 (t,  $J_{CP} = 20.1 \text{ Hz}$ ) (dppe). <sup>31</sup>P{<sup>1</sup>H} NMR: 60.44 (d,  $J_{PP} = 47.56$  Hz, 1P), 59.77 (d,  $J_{\rm PP} = 47.56$  Hz, 1P). IR (KBr pellet, cm<sup>-1</sup>): 3020 m, 1559 s, 1480 w, 1463 s, 1434 vs, 1310 s, 1188 w, 1100 s, 1026 m, 876 m, 851 w, 820 s, 737 s, 689 vs, 528 vs, 480 vs, 432 w, 395 w, 372 m.

Reaction of Ni(dppe) organodichalocogenide complexes with DMAD. In a typical reaction excess DMAD (2 cm<sup>3</sup>, 16.27 mmol) and Ni(dppe)(SC<sub>6</sub>H<sub>4</sub>O) (0.20 g, 0.34 mmol) solution in toluene/CH<sub>2</sub>Cl<sub>2</sub> (1:1) (50 cm<sup>3</sup>) was refluxed for 24 h. The dark orange solution obtained was concentrated to about 5 cm<sup>3</sup> and chromatographed (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/ether 1:4) to yield 0.40 g (0.94 mmol) of hexamethylbenzene hexacarboxylate, C<sub>6</sub>(CO<sub>2</sub>Me)<sub>6</sub>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.88 (s, 18H). <sup>13</sup>C NMR: 165.2 (s), 133.9 (s), 53.5 (s). IR (KBr pellet cm<sup>-1</sup>): 3012 m, 2958 s, 1738 vs, 1576 w, 1445 vs, 1413 s, 1363 s, 1332 s, 1235 vs, 1182 vs, 1160 s, 1122 m, 985 vs, 906 w, 872 s, 860 vs, 849 vs, 828 s, 805 w, 787 w, 757 m, 618 s, 603 m, 471 w. MS (EI): m/z (relative intensity) 426 (2) (M<sup>+</sup>), 395 (100) (M<sup>+</sup> – OMe). The other complexes were reacted with DMAD using the same number of moles of nickel complex (0.34 mmol) and DMAD (16.27 mmol). The number of moles of HMBC isolated were **3** (0.23 mmol), **4** (0.52 mmol) and **5** (2.26 mmol).

### Crystal structure determination of 2

Single crystals of 2 suitable for crystal structural determination were obtained by slow diffusion of hexane into a  $CH_2Cl_2$  solution of **2** at room temperature. dark rectangular plate crystal of size A  $0.70 \times 0.22 \times 0.11$  mm was mounted in a sealed capillary tube for data collection. All geometric and intensity data were collected on a Siemens SMART diffractometer with a CCD detector. Crystal data for  $C_{32}H_{28}OP_2SNi$  (*Mr* = 581.25): orthorhombic, Pbca; a = 12.5385(6) Å, b = 15.1818(2) Å, c = 29.496(2) Å,  $V = 5614.7(5) \text{ Å}^3$ ; Z = 8;  $D_{\text{calc}} = 1.375 \text{ Mg m}^{-3}$ ; Mo- $K_x$  radiation ( $\lambda = 0.71073$  Å); T = 298;  $\theta = 1.38-$ 28.29 , 10 s/frame exposure ; 0.3 /frame ; 6563 independent reflections collected, 4970 unique. Full matrix least-squares refinement [17] of 446 parameters on  $F^2$ gave  $R_1 = 0.0698$ .  $wR_2 = 0.1746$ , GoF = 1.253. Max  $\Delta F 0.42 \text{ e}\text{\AA}^{-3}$ , min  $-0.25 \text{ e}\text{\AA}^{-3}$ . An absorption correction based on multiple redundant data analysis was applied [18].

Supplementary material. Further crystallographic details can be obtained on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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