Supplementary Material (ESI) for Chemical Communications

Supporting Information

White Phosphorus as Single Source of "P" in the Synthesis of Metal Phosphide

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General Methods. All reactions were carried out under nitrogen atmosphere using standard air-free techniques.[1] All solvents used were of analytical grade and were dried and degassed before use.[2] Trioctylphosphine oxide (TOPO, Aldrich, 90%), oleylamine (Aldrich, 70%) and tributylphosphine (Aldrich, 97%) were used in the preparation described here without further purification. $[Ni(COD)_2]$ was prepared following the literature process.[3] NMR spectra were recorded on a Bruker AMX-300 spectrometer. The ^{1}H and ^{13}C resonances of the solvent were used as the internal standard, and the chemicals shift are reported relative to TMS.

Instrumentation

X-ray Diffraction:

Data were collected on a Nonius Kappa CCD diffractometer at 150 K using a Mo K (λ = 0.71073 Å). X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structure was solved using SIR 97[4] and Shelxl-97.[5] ORTEP drawings were made using ORTEP III for Windows.[6]

Transmission Electron Microscope (TEM):

The transmission electron microscope (Philips CM30) with an accelerating voltage of 300 kV was used for the imaging work. TEM micrographs were processed with a slow scan CCD camera. The images were analysed with Digital Micrograph software. TEM samples were prepared by dropping the hexane solution onto a copper grid (200 mesh) coated with carbon film.

References

[1] Shriver, D. F. *The Manipulation of Air-Sensitive Compounds,* 2nd ed.; Wiley Interscience: New York, 1986.

[2] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980.

[3] Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, *55*, 4229.

[4] Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97, an integrated package computer programs for the solution and refinement of crystal structure using single crystal data .

[5] Sheldrick, G. M. SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.

[6] Farrugia, L. J. ORTEP-3 for windows, Department of Chemistry, University of Glasgow.

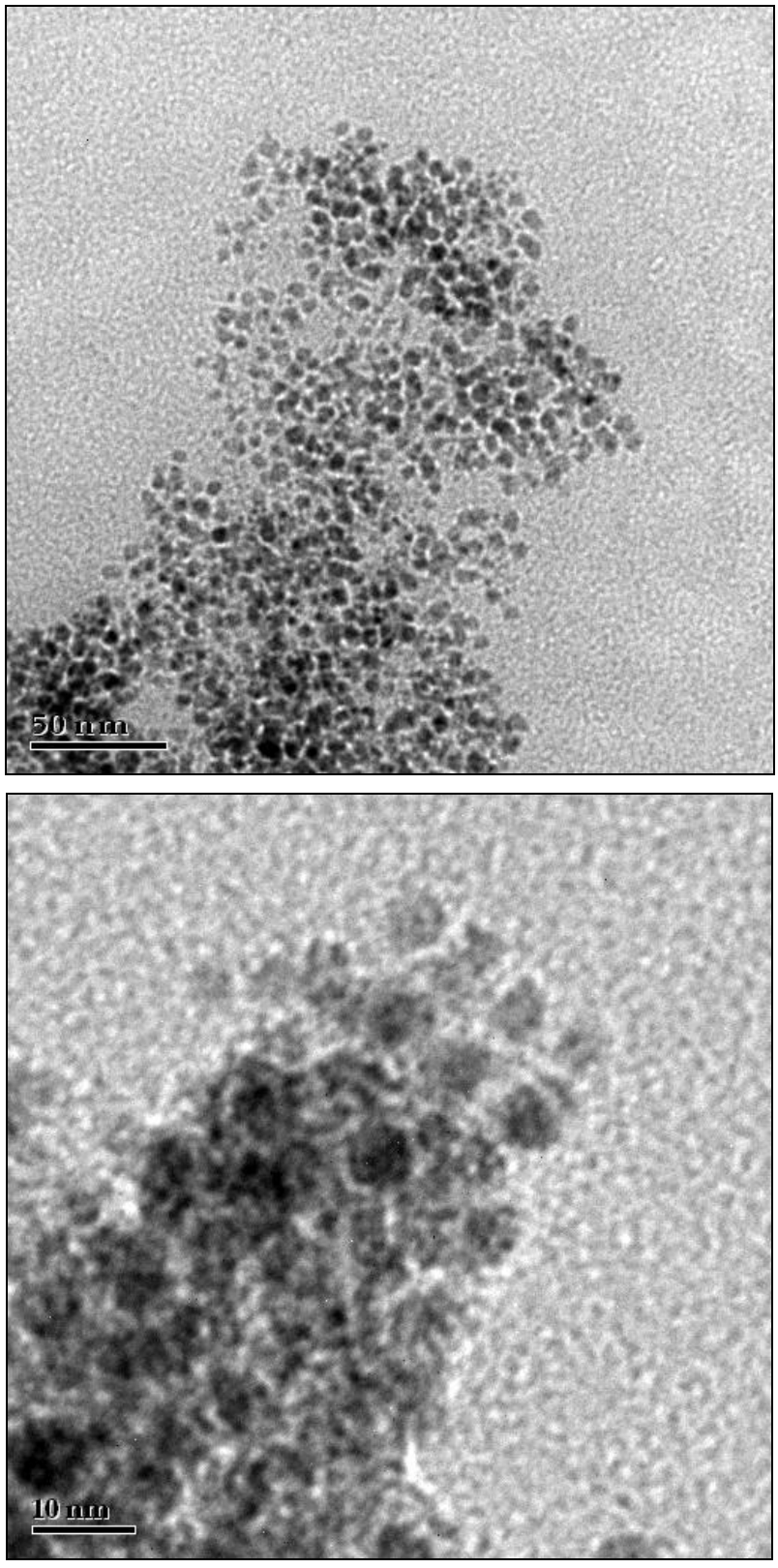

Figure S1. TEM micrograph of the Ni_2P stabilized with TOPO.

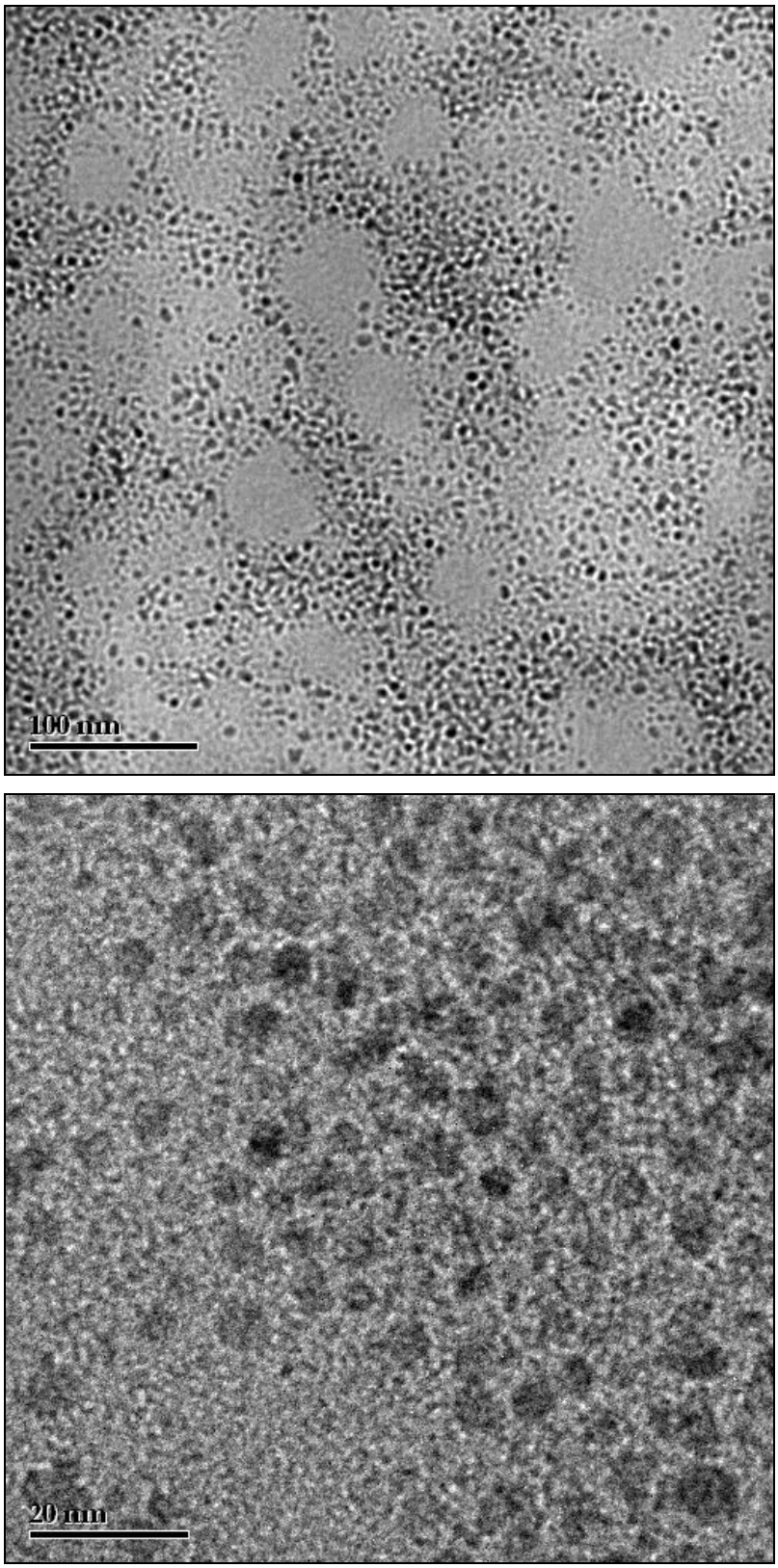

Figure S2. TEM micrograph of the Ni_2P stabilized with oleylamine.

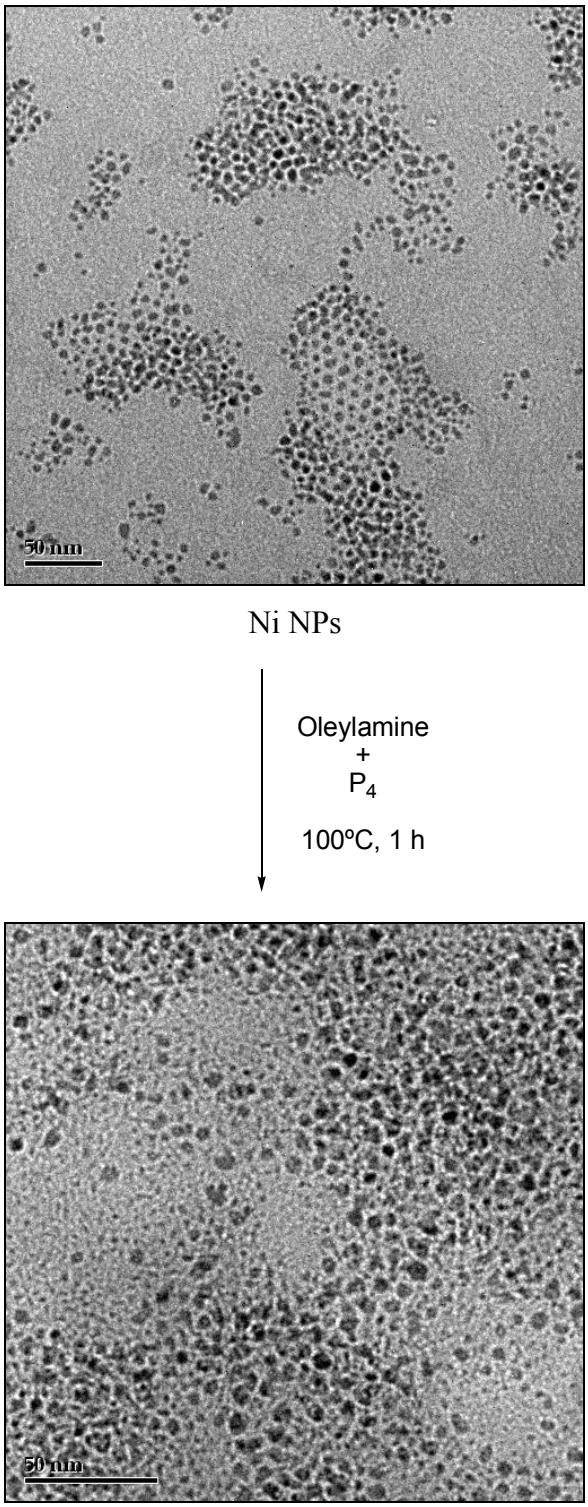

Figure S3. Reaction between Ni NPs and P_4 in oleylamine to yield Ni_2P NPs.

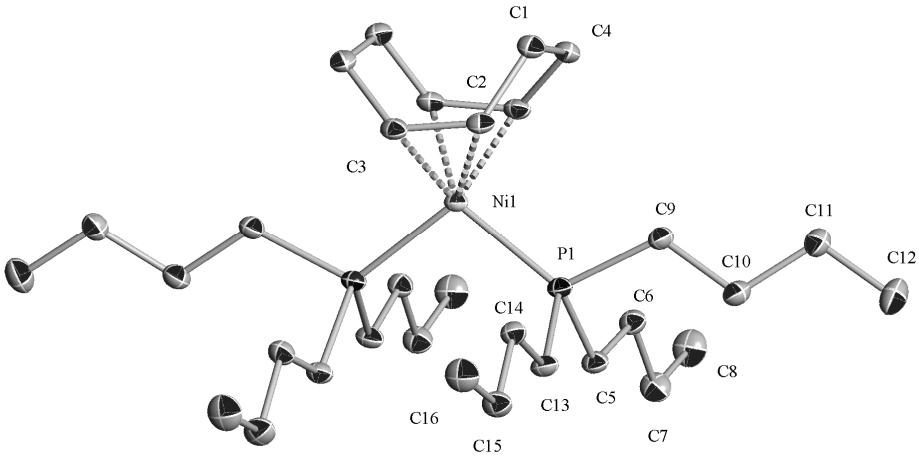

Figure S4. ORTEP Plot of $[Ni(COD)(PBu_3)_2]$

Table 1. Crystal data for $[Ni(COD)(PBu_3)_2]$.

Compound	$[Ni(COD)(PBu_3)_2]$
Molecular formula	$C_{32}H_{66}NiP_2$
Molecular weight	285.75
Crystal habit	Yellow Plate
Crystal dimensions(mm)	0.30x0.16x0.08
Crystal system	monoclinic
Space group	C2/c
a (Å)	21.777(1)
b (Å)	8.967(1)
c (Å)	17.218(1)
α (°)	90.00
β (°)	90.769(1)
γ (°)	90.00
V(Å^3)	3361.9(5)
Z	8
d(g-cm^{-3})	1.129
F(000)	1264
μ (cm^{-1})	0.690
Absorption corrections	multi-scan ; 0.8197 min, 0.9469 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-25 30 ; -11 12 ; -20 24
Reflections measured	15342
Unique data	4911
Rint	0.0274
Reflections used	4007
Criterion	$I > 2\sigma(I)$
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	163
Reflections / parameter	24
wR2	0.0994
R1	0.0371
Weights a, b	0.0474 ; 1.4878
GoF	1.073
difference peak / hole (e Å^{-3})	0.514(0.057) / -0.469(0.057)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for irg05007

atom	x	y	z	U(eq)
Ni(1)	0	673(1)	2500	23(1)
P(1)	415(1)	2157(1)	1652(1)	24(1)
C(1)	158(1)	-2221(2)	1646(1)	33(1)
C(2)	-292(1)	-932(2)	1690(1)	28(1)
C(3)	-724(1)	-813(2)	2272(1)	28(1)
C(4)	773(1)	-1930(2)	2076(1)	32(1)
C(5)	947(1)	3644(2)	1973(1)	29(1)
C(6)	1546(1)	3110(2)	2351(1)	31(1)
C(7)	1943(1)	4390(2)	2640(1)	39(1)
C(8)	2530(1)	3875(3)	3045(1)	50(1)
C(9)	871(1)	1234(2)	893(1)	29(1)
C(10)	1164(1)	2170(2)	254(1)	33(1)
C(11)	1608(1)	1266(2)	-231(1)	35(1)
C(12)	1907(1)	2190(2)	-867(1)	48(1)
C(13)	-107(1)	3362(2)	1073(1)	29(1)
C(14)	-653(1)	2604(2)	679(1)	28(1)
C(15)	-1074(1)	3725(2)	273(1)	35(1)
C(16)	-1641(1)	3037(2)	-105(1)	46(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for [Ni(COD)(PBu_3)$_2$]

Ni(1)-C(2)#2	2.097(1)	Ni(1)-C(2)	2.097(1)
Ni(1)-C(3)	2.097(1)	Ni(1)-C(3)#2	2.097(1)
Ni(1)-P(1)	2.1799(4	Ni(1)-P(1)#2	2.1799(4)
P(1)-C(5)	1.848(2)	P(1)-C(9)	1.849(2)
P(1)-C(13)	1.850(2)	C(1)-C(2)	1.518(2)
C(1)-C(4)	1.543(2)	C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900	C(2)-C(3)	1.386(2)
C(2)-H(2)	0.9500	C(3)-C(4)#2	1.510(2)
C(3)-H(3)	0.9500	C(4)-C(3)#2	1.510(2)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(5)-C(6)	1.526(2)	C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900	C(6)-C(7)	1.518(2)
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-C(8)	1.519(2)	C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900	C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800	C(8)-H(8C)	0.9800
C(9)-C(10)	1.530(2)	C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900	C(10)-C(11)	1.521(2)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.525(2)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800
C(13)-C(14)	1.521(2)	C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900	C(14)-C(15)	1.523(2)
C(14)-H(14A)	0.9900	C(14)-H(14B)	0.9900
C(15)-C(16)	1.520(2)	C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900	C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800	C(16)-H(16C)	0.9800

C(2)#2-Ni(1)-C(2)	93.32(8)	C(2)#2-Ni(1)-C(3)	84.78(6)
C(2)-Ni(1)-C(3)	38.60(6)	C(2)#2-Ni(1)-C(3)#2	38.60(6)
C(2)-Ni(1)-C(3)#2	84.78(6)	C(3)-Ni(1)-C(3)#2	101.06(8)
C(2)#2-Ni(1)-P(1)	137.69(4)	C(2)-Ni(1)-P(1)	95.62(4)
C(3)-Ni(1)-P(1)	125.39(4)	C(3)#2-Ni(1)-P(1)	101.33(4)
C(2)#2-Ni(1)-P(1)#2	95.62(4)	C(2)-Ni(1)-P(1)#2	137.69(4)
C(3)-Ni(1)-P(1)#2	101.33(4)	C(3)#2-Ni(1)-P(1)#2	125.39(4)
P(1)-Ni(1)-P(1)#2	104.81(2)	C(5)-P(1)-C(9)	101.16(7)
C(5)-P(1)-C(13)	96.76(7)	C(9)-P(1)-C(13)	102.33(7)
C(5)-P(1)-Ni(1)	120.26(5)	C(9)-P(1)-Ni(1)	115.61(5)
C(13)-P(1)-Ni(1)	117.40(5)	C(2)-C(1)-C(4)	113.9(1)
C(2)-C(1)-H(1A)	108.8	C(4)-C(1)-H(1A)	108.8
C(2)-C(1)-H(1B)	108.8	C(4)-C(1)-H(1B)	108.8
H(1A)-C(1)-H(1B)	107.7	C(3)-C(2)-C(1)	122.6(1)
C(3)-C(2)-Ni(1)	70.70(8)	C(1)-C(2)-Ni(1)	111.4(1)
C(3)-C(2)-H(2)	118.7	C(1)-C(2)-H(2)	118.7
Ni(1)-C(2)-H(2)	88.0	C(2)-C(3)-C(4)#2	122.9(1)
C(2)-C(3)-Ni(1)	70.69(8)	C(4)#2-C(3)-Ni(1)	110.1(1)
C(2)-C(3)-H(3)	118.6	C(4)#2-C(3)-H(3)	118.6
Ni(1)-C(3)-H(3)	89.2	C(3)#2-C(4)-C(1)	113.4(1)
C(3)#2-C(4)-H(4A)	108.9	C(1)-C(4)-H(4A)	108.9
C(3)#2-C(4)-H(4B)	108.9	C(1)-C(4)-H(4B)	108.9
H(4A)-C(4)-H(4B)	107.7	C(6)-C(5)-P(1)	115.5(1)
C(6)-C(5)-H(5A)	108.4	P(1)-C(5)-H(5A)	108.4
C(6)-C(5)-H(5B)	108.4	P(1)-C(5)-H(5B)	108.4
H(5A)-C(5)-H(5B)	107.5	C(7)-C(6)-C(5)	112.5(1)
C(7)-C(6)-H(6A)	109.1	C(5)-C(6)-H(6A)	109.1
C(7)-C(6)-H(6B)	109.1	C(5)-C(6)-H(6B)	109.1
H(6A)-C(6)-H(6B)	107.8	C(6)-C(7)-C(8)	113.1(2)
C(6)-C(7)-H(7A)	109.0	C(8)-C(7)-H(7A)	109.0
C(6)-C(7)-H(7B)	109.0	C(8)-C(7)-H(7B)	109.0
H(7A)-C(7)-H(7B)	107.8	C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5	H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5	H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5	C(10)-C(9)-P(1)	119.7(1)
C(10)-C(9)-H(9A)	107.4	P(1)-C(9)-H(9A)	107.4

C(10)-C(9)-H(9B)	107.4	P(1)-C(9)-H(9B)	107.4
H(9A)-C(9)-H(9B)	106.9	C(11)-C(10)-C(9)	112.1(1)
C(11)-C(10)-H(10A)	109.2	C(9)-C(10)-H(10A)	109.2
C(11)-C(10)-H(10B)	109.2	C(9)-C(10)-H(10B)	109.2
H(10A)-C(10)-H(10B)	107.9	C(10)-C(11)-C(12)	112.6(2)
C(10)-C(11)-H(11A)	109.1	C(12)-C(11)-H(11A)	109.1
C(10)-C(11)-H(11B)	109.1	C(12)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8	C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(14)-C(13)-P(1)	116.7(1)
C(14)-C(13)-H(13A)	108.1	P(1)-C(13)-H(13A)	108.1
C(14)-C(13)-H(13B)	108.1	P(1)-C(13)-H(13B)	108.1
H(13A)-C(13)-H(13B)	107.3	C(13)-C(14)-C(15)	111.8(1)
C(13)-C(14)-H(14A)	109.3	C(15)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14B)	109.3	C(15)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	107.9	C(16)-C(15)-C(14)	114.1(2)
C(16)-C(15)-H(15A)	108.7	C(14)-C(15)-H(15A)	108.7
C(16)-C(15)-H(15B)	108.7	C(14)-C(15)-H(15B)	108.7
H(15A)-C(15)-H(15B)	107.6	C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5		

Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z	2: -x, y, -z+1/2	3: x+1/2, y+1/2, z
4: -x+1/2, y+1/2, -z+1/	5: -x, -y, -z	6: x, -y, z-1/2
7: -x+1/2, -y+1/2, -z	8: x+1/2, -y+1/2, z-1/2	

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for [Ni(COD)(PBu_3)$_2$]

atom	U11	U22	U33	U23	U13	U12
Ni(1)	23(1)	16(1)	28(1)	0	-1(1)	0
P(1)	25(1)	18(1)	30(1)	1(1)	-1(1)	-2(1)
C(1)	39(1)	24(1)	35(1)	-4(1)	3(1)	-1(1)
C(2)	32(1)	19(1)	33(1)	-2(1)	-3(1)	-4(1)
C(3)	26(1)	20(1)	37(1)	-3(1)	-3(1)	-3(1)
C(4)	32(1)	22(1)	41(1)	1(1)	5(1)	5(1)
C(5)	29(1)	22(1)	35(1)	-1(1)	-1(1)	-4(1)
C(6)	29(1)	28(1)	35(1)	0(1)	-1(1)	-4(1)
C(7)	32(1)	38(1)	47(1)	-8(1)	-6(1)	-6(1)
C(8)	37(1)	62(1)	52(1)	-4(1)	-11(1)	-9(1)
C(9)	31(1)	25(1)	30(1)	2(1)	2(1)	-2(1)
C(10)	39(1)	29(1)	32(1)	3(1)	1(1)	-6(1)
C(11)	34(1)	37(1)	33(1)	0(1)	2(1)	-6(1)
C(12)	49(1)	58(1)	38(1)	0(1)	8(1)	-17(1)
C(13)	30(1)	21(1)	37(1)	4(1)	-2(1)	-2(1)
C(14)	29(1)	26(1)	30(1)	2(1)	0(1)	0(1)
C(15)	33(1)	32(1)	39(1)	4(1)	-4(1)	4(1)
C(16)	36(1)	52(1)	51(1)	2(1)	-11(1)	3(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for irg05007

atom	x	y	z	U(eq)
H(1A)	242	-2433	1094	39
H(1B)	-36	-3119	1870	39
H(2)	-278	-177	1304	34
H(3)	-1000	6.0000	2259	34
H(4A)	929	-2885	2290	38
H(4B)	1076	-1562.9999	1698	38
H(5A)	1049	4267	1517	34
H(5B)	731	4290	2348	34
H(6A)	1449	2448	2793	37
H(6B)	1779	2518	1969	37
H(7A)	1703	5004	3005	47
H(7B)	2052	5030	2193	47
H(8A)	2426	3251	3492	75
H(8B)	2764	4745	3224	75
H(8C)	2777	3297	2681	75
H(9A)	1205	675	1158	34
H(9B)	603	487	635	34
H(10A)	836	2579	-89	40
H(10B)	1386	3019	493	40
H(11A)	1385	419	-473	42
H(11B)	1932	850	113	42
H(12A)	1592	2513	-1242	72
H(12B)	2214	1583	-1132	72
H(12C)	2106	3066	-635	72
H(13A)	-266	4151	1420	35
H(13B)	137	3861	668	35
H(14A)	-889	2049	1071	34
H(14B)	-502	1878	293	34
H(15A)	-1206	4477	658	42
H(15B)	-837	4252	-130	42
H(16A)	-1516	2309	-497	70
H(16B)	-1887	3822	-354	70
H(16C)	-1885	2538	291	70