Supporting information

Tridentate NNN ligand associating amidoquinoline and iminophosphorane: synthesis and coordination to Pd and Ni centers.

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Table of content

X-ray diffraction data

Table S1 : Crystallographic Data for $\mathbf{L^{Ph}}$, $\mathbf{L^{Cy}}$, **2**, and **3**.

	$\mathbf{L^{Ph}}$	$\mathbf{L^{Cy}}$	**2**	**3**
Formula	$C_{29}H_{24}N_3OP$	$C_{29}H_{42}N_3OP$	$2(C_{29}H_{23}ClN_3OPPd)$, $3(CH_2Cl_2)$, $C_4H_{10}O$	$C_{65}H_{62}Cl_8N_6Ni_2O_3P_2$
Mw	461.48	479.62	1533.54	1438.16
Space group	P $2_1/n$	P $2_1/n$	P -1	P-1
V (Å^3)	2341.0(3)	2653.8(2)	3344.3(3)	3227.7(16)
a (Å)	9.3247(6)	9.8348(5)	13.2971(6)	10.292(3)
b (Å)	26.126(2)	11.8002(6)	13.6091(7)	16.074(5)
c (Å)	10.0824(8)	22.9353(12)	20.9412(11)	21.287(6)
α (deg)	90	90	82.196(2)	67.871(8)
β (deg)	107.619(2)	94.410(2)	76.924(2)	89.998(8)
γ (deg)	90	90	65.087(2)	82.260(9)
Z	4	4	2	2
d (g.cm^{-3})	1.309	1.200	1.523	1.480
F(000)		1040	1552	1480.0
θ_{max}	27.590	27.550	27.587	26.022
Rflns measd	22727	39472	77881	12711
Unique data	5368	6099	15451	8969
R_{int}	0.0557	0.0422	0.0619	
wR2	0.1053	0.1125	0.1193	0.3086
R1	0.0416	0.0375	0.0425	0.1190
GoF	0.999	0.997	1.019	1.304
CCDC number	1972825	1972826	1972830	1972827

Table S2 : Crystallographic Data for **5**, **6**, **[(L^{Cy})$_2$Ni]**

	5	**6**	**[L^{Cy}_2Ni]**
Formula	$C_{29}H_{24}N_3NiO\ P$	$C_{30}H_{24}N_3NiO_2P$	$C_{58}H_{82}N_6NiO_2P_2$
Mw	520.19	548.20	1015.94
Space group	P -1	$P2_1/n$	P b c n
V (Å^3)	2395.9(4)	2479.2(3)	6046.1(17)
a (Å)	11.3967(11)	9.9647(6)	19.191(3)
b (Å)	15.6739(17)	20.7694(13)	18.633(3)
c (Å)	15.6977(16)	12.2299(7)	16.908(3)
α (deg)	115.322(3)	90	90
β (deg)	103.355(3)	101.619(2)	90
γ (deg)	96.289(3)	90	90
Z	4	4	4
d (g.cm^{-3})	1.442	1.469	1.116
F(000)	1080	1136	2184
θ_{max}	27.589	27.544	24.710
Rflns measd	56008	42972	80960
Unique data	11057	5705	5154
R_{int}	0.1036	0.0426	0.3216
wR2	0.0873	0.0856	0.2054
R1	0.0346	0.0358	0.0792
GoF	1.030	1.118	1.183
CCDC number	1972829	1972828	1972824

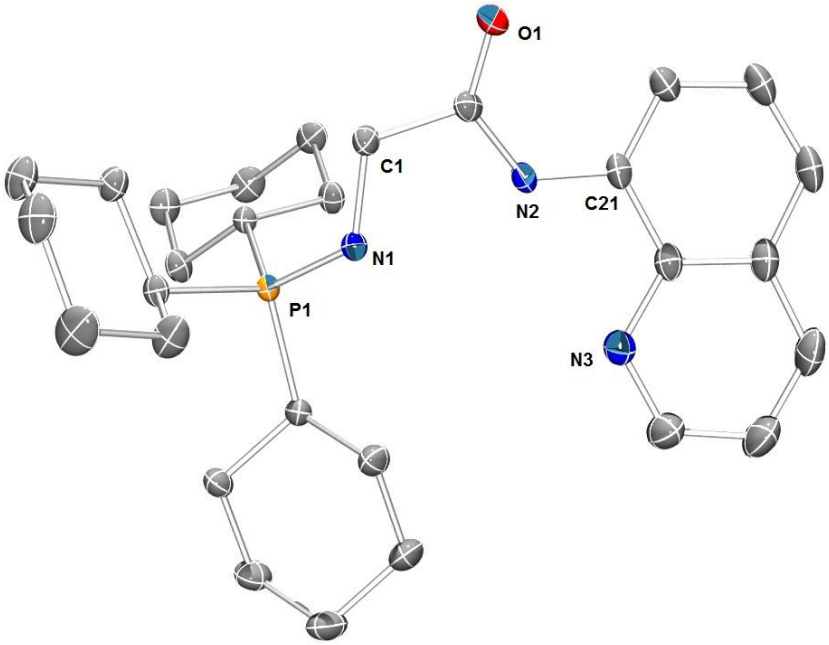


Figure S1: ORTEP de $\mathbf{L^{Cy}H}$. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): P1–N1 1.580(1), O1–C2 1.227(2), N1–C1 1.446(2), N2–C2 1.351(2), N2–C21 1.402(2), C1–C2 1.525(2), C1–N1–P1 122.72(8), C2–N2–C21 127.6(1), N1–C1–C2 112.7(1), O1–C2–N2 125.4(1), O1–C2–C1 121.1(1), N2–C2–C1 113.5(1).

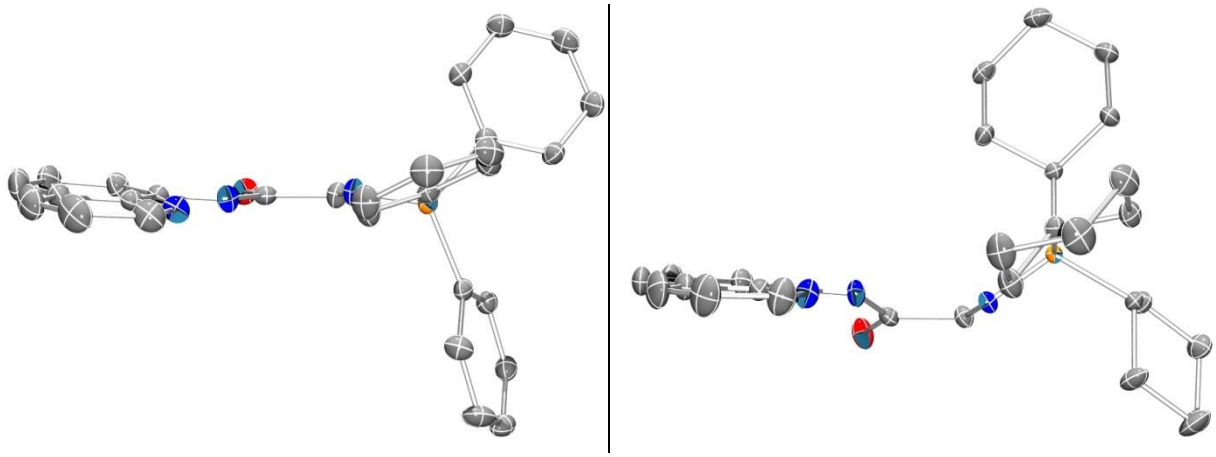


Figure S2. ORTEP plot of de $\mathbf{L^{Ph}}$ (left) et $\mathbf{L^{Cy}}$ (right) perpendicularly to the quinoline plane.

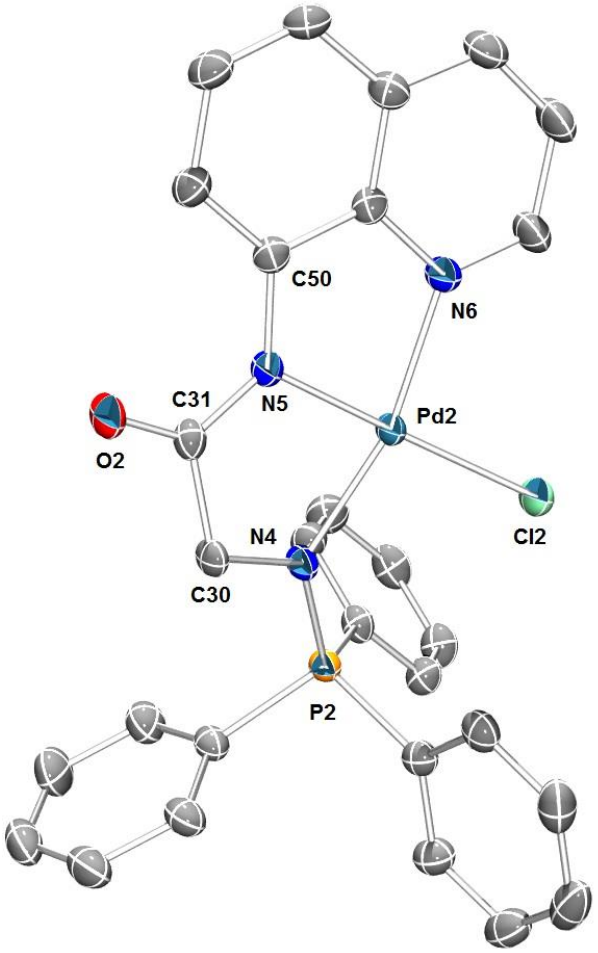


Figure S3. ORTEP plot of the second molecule of **2:** 3 dichloromethane, one ether molecules and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pd2–N4 2.028(3), Pd2–N5 1.954(3), Pd2–N6 2.022(3), Pd2–Cl2 2.322(1), P2–N6 1.604(3), O2–C31 1.231(4), N5–C31 1.347(4, N5–C35 1.396(4), N6–C40 1.476(4), C31–C40 1.514(4, N5–Pd2–N6 82.1(1, N5–Pd2–N4 82.1(1, N6–Pd2–N4 163.9(1), N5–Pd2–Cl2 177.67(8), N6–Pd2–Cl2 99.18(8), N4–Pd2–Cl2 96.73(8), C31–N5–C50 126.0(3, C39–N5–Pd2 118.2(2), C35–N5–Pd2 115.3(2), C30–N6–P2 122.4(2), C30–N6–Pd2 118.2(2)P2–N6–Pd2 126.7(2), N6-C30-C31 111.8(3).

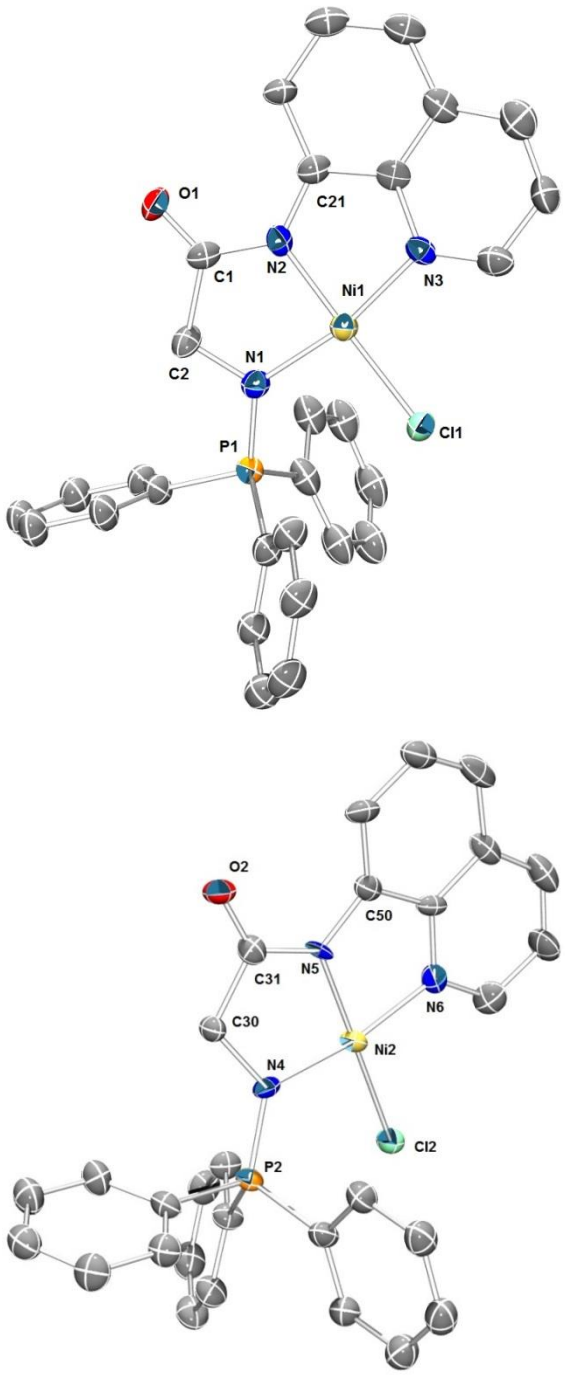


Figure S4. ORTEP plot of the 2 independent **3** molecules in the unit cell. 3 dichloromethane, one ether molecules and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–Cl1 2.189(3), Ni1–N3 1.906(7), Ni1–N1 1.907(7), Ni1–N2 1.871(7), P1–N1 1.600(8), O1–C1 1.211(11), N1–C2 1.493(11), N2–C1 1.375(12), N2–C21 1.362(12), C1–C2 1.505(13), N3–Ni1–N1 168.4(3), N2–Ni1–Cl1 178.3(2), P1–N1–Ni1 127.4(4), C2–N1–Ni1 112.4(5), C2–N1–P1 119.9(6), C1–N2–Ni1 118.3(6), C21–N2–C1 126.1(8), O1–C1–N2 125.0(8), N2–C1–C2 111.8(8), N1–C2–C1 110.2(8) ; Ni2–Cl2 2.182(2), Ni2–N6 1.912(7), Ni2–N4 1.899(7), Ni2–N5 1.888(6), P2–N4 1.598(7), O2–C31 1.229(11), N4–C30 1.485(11), N5–C31 1.305(11), N5–C50 1.386(11), C30–C31 1.510(12), N6–Ni2–N4 168.8(3), N5–Ni2–Cl2 178.9(2), P2–N4–Ni2 125.5(4), C30–N4–Ni2 112.9(5), C30–N4–P2 121.6(6), C31–N5–Ni2 119.3(6), C31–N5–C50 127.5(7), O2–C31–N5 126.1(8), N5–C31–C30 112.9(7), N4–C30–C31 109.4(7).

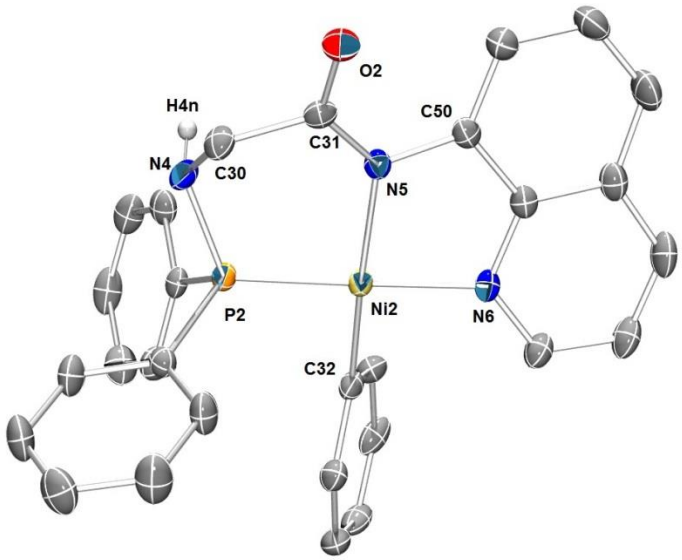


Figure S5 ORTEP plot of the second molecule of **5:** All hydrogen atoms (except that of the aminophosphine) were omitted for clarity. Selected bond lengths (Å) and angles (°):Ni2–C32 1.895(2), Ni2–N6 1.946(2), Ni2–N5 1.959(2), Ni2–P2 2.1212(6), P2–N4 1.663(2), P1–C9 1.824(2), O2–C31 1.240(2), N4–C30 1.462(2), N5–C31 1.360(2), N5–C50 1.419(2), C30–C31 1.525(3), C32–Ni2–N6 91.99(7), C32–Ni2–N5 171.57(8), N6–Ni2–N5 83.87(7), C32–Ni2–P2 84.72(6), N6–Ni2–P2 176.63(5), N3–Ni5–P2 99.31(5), N4–P2–C24 102.3(1), N4–P2–Ni2 107.22(6), C30–N4–P2 115.0(1), C31–N5–C50 119.4(2), C31–N5–Ni2 129.0(1), C50–N5–Ni2 111.5(1), N4–C30–C31 113.2(2), N5–C31–C30 116.6(2).

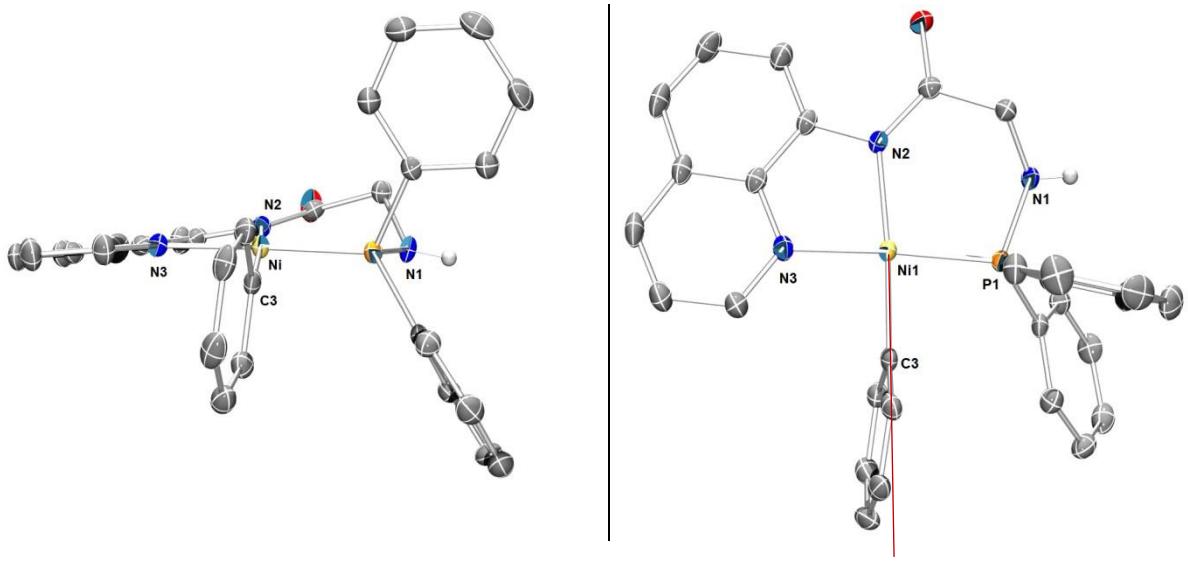


Figure S6. ORTEP plot of **5** along N3-Ni1-N2 plane and from the top of this plane: all hydrogen atoms (except that of the aminophosphine) were omitted for clarity.

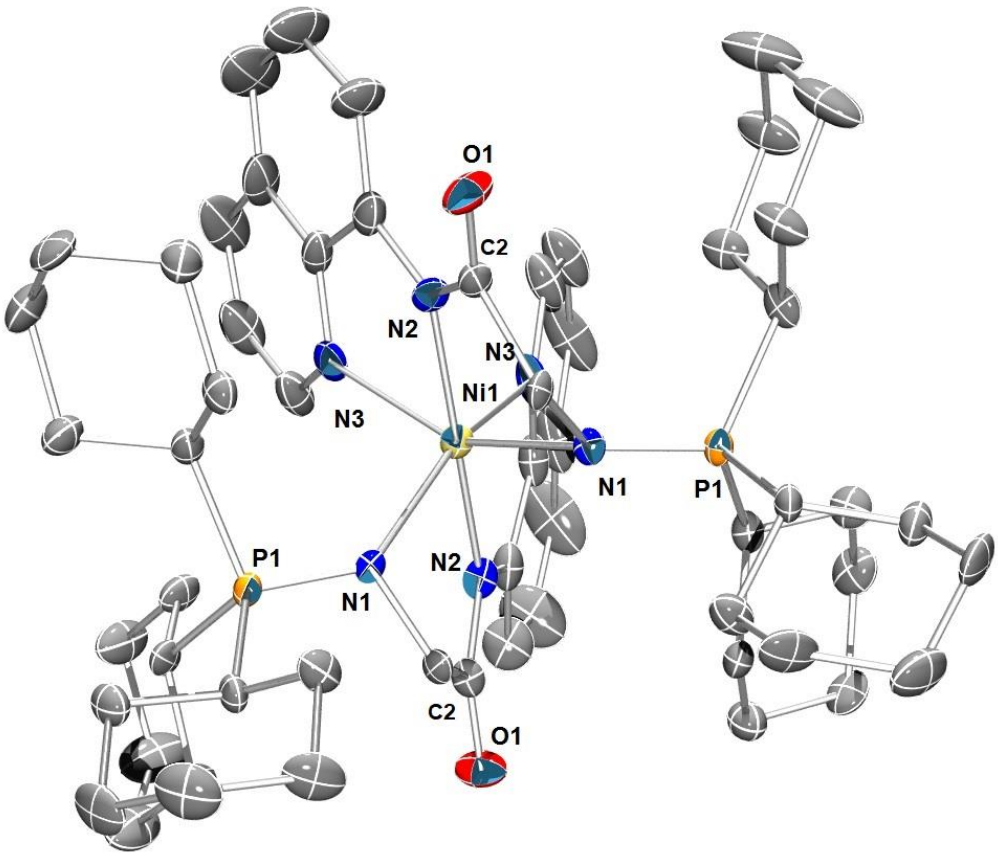


Figure S7. ORTEP of **[(L^{Cy})$_2$Ni]**. All hydrogen atoms (except that of the aminophosphine) were omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1 2.252(5), Ni1–N2 2.006(4), Ni1–N3 2.193(4), P1–N3 1.596(4), N2–Ni1–N1 76.81(18), N2–Ni1–N3 79.47(16), N3–Ni1–N1 155.16(15).

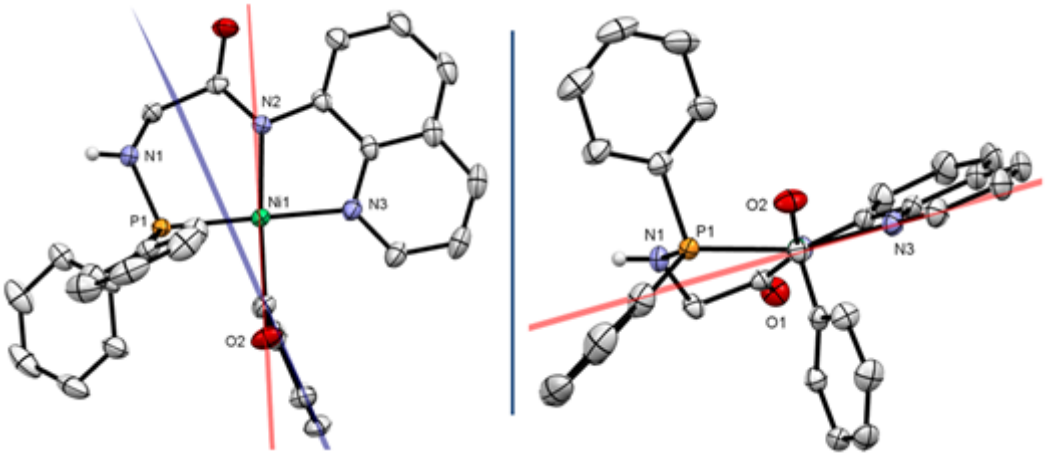
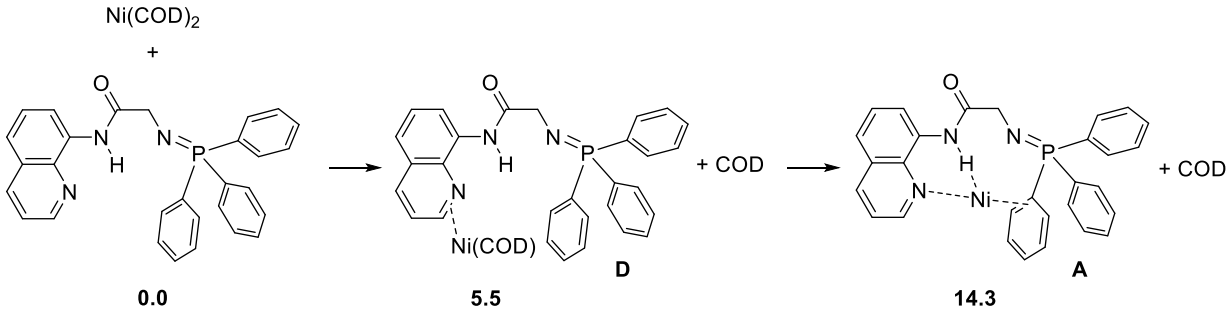


Figure S8. ORTEP plot of **6** from the top of the along N3-Ni1-N2 plane (left) and all this plane (right) all hydrogen atoms (except that of the aminophosphine) were omitted for clarity.

Calculations

Complete Gaussian reference:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, revision D.01, Gaussian, Inc.,
Wallingford CT, 2013.



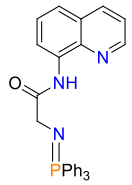
Scheme S1. Free Energies of the COD Ligand Exchanges (ΔG_{333}, kcal/mol)

Table S3. M06 Energies (Hartree) and Imaginary Frequencies (cm^{-1}) of the Computed Species

$Ni(COD)_2$ E(RM06) = -2132.14534609	**$L^{Ph}H$** E(RM06) = -1699.88591473
D E(RM06) = -3520.12766454	COD E(RM06) = -311.890005537
A E(RM06) = -3208.19622910	**TS_{AB}** E(RM06) = -3208.17324183 Frequency -948.3742
B E(RM06) = -3208.20530950	**TS_{BC}** E(RM06) = -3208.19749403 Frequency -93.2335
C E(RM06) = -3208.24798643	

NMR-spectra

a



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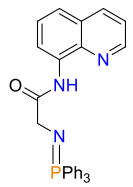
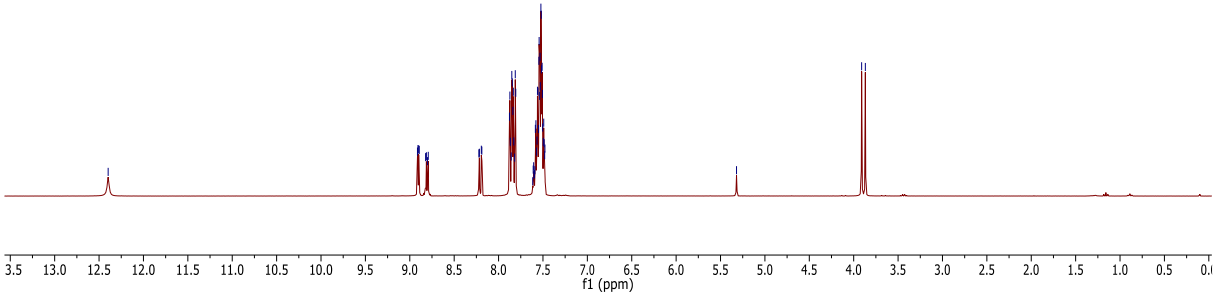




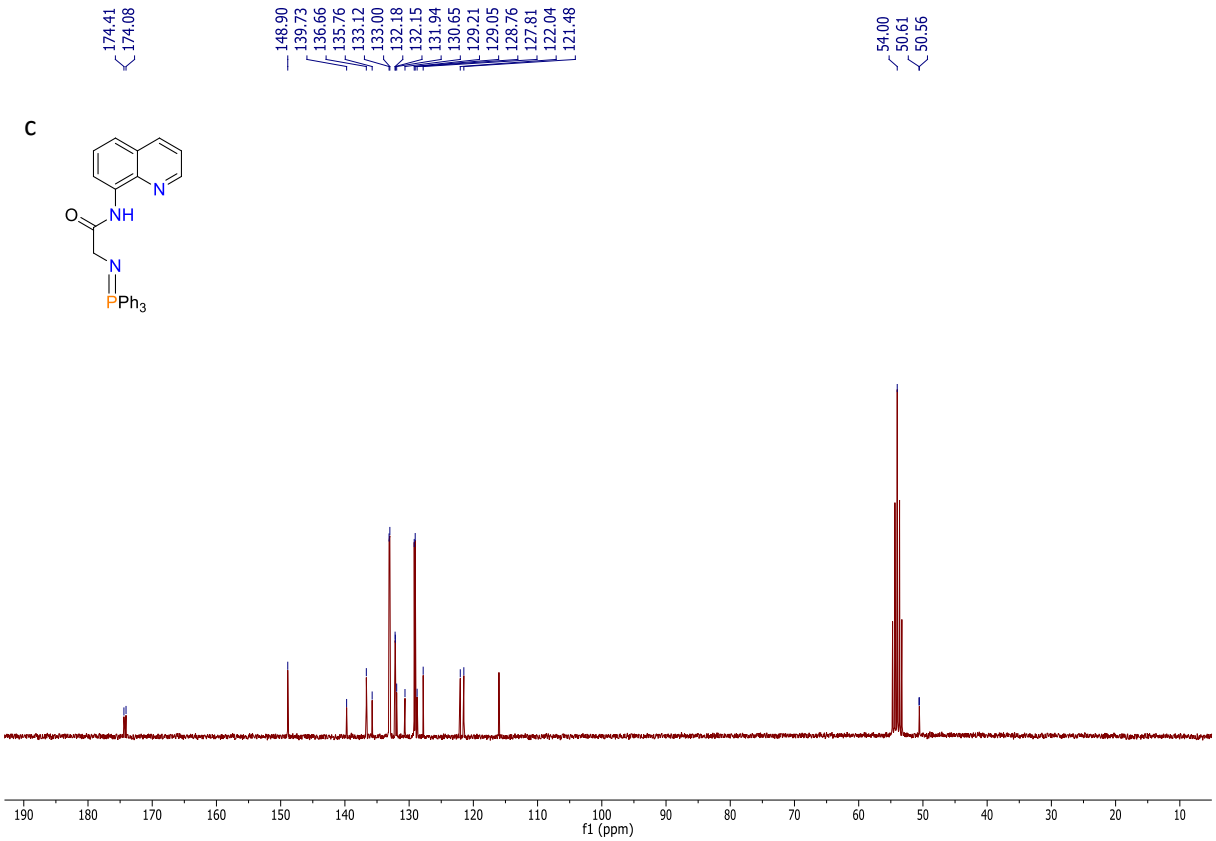
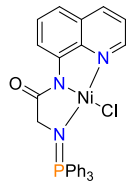


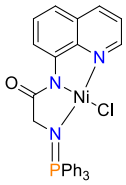
Figure S9. $^{31}P\{^{1}H\}$ (a), ^{1}H (b), ^{13}C (c) NMR spectra of **$L^{Ph}H$**

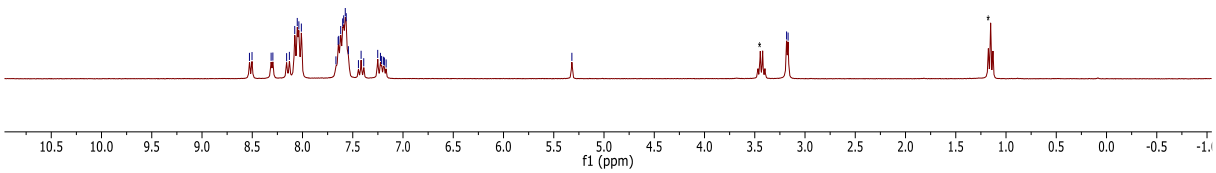
a


O
N
Ni
Cl
N
PPh3

35.94
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)
8.53 8.50 8.31 8.30 8.16 8.13 8.08 8.05 8.04 8.01 7.67 7.65 7.64 7.62 7.60 7.59 7.57 7.57 7.54 7.44 7.42 7.39 7.25 7.22 7.21 7.20 7.19 7.17 5.32
3.18 3.17

b


O
N
Ni
Cl
N
PPh3


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

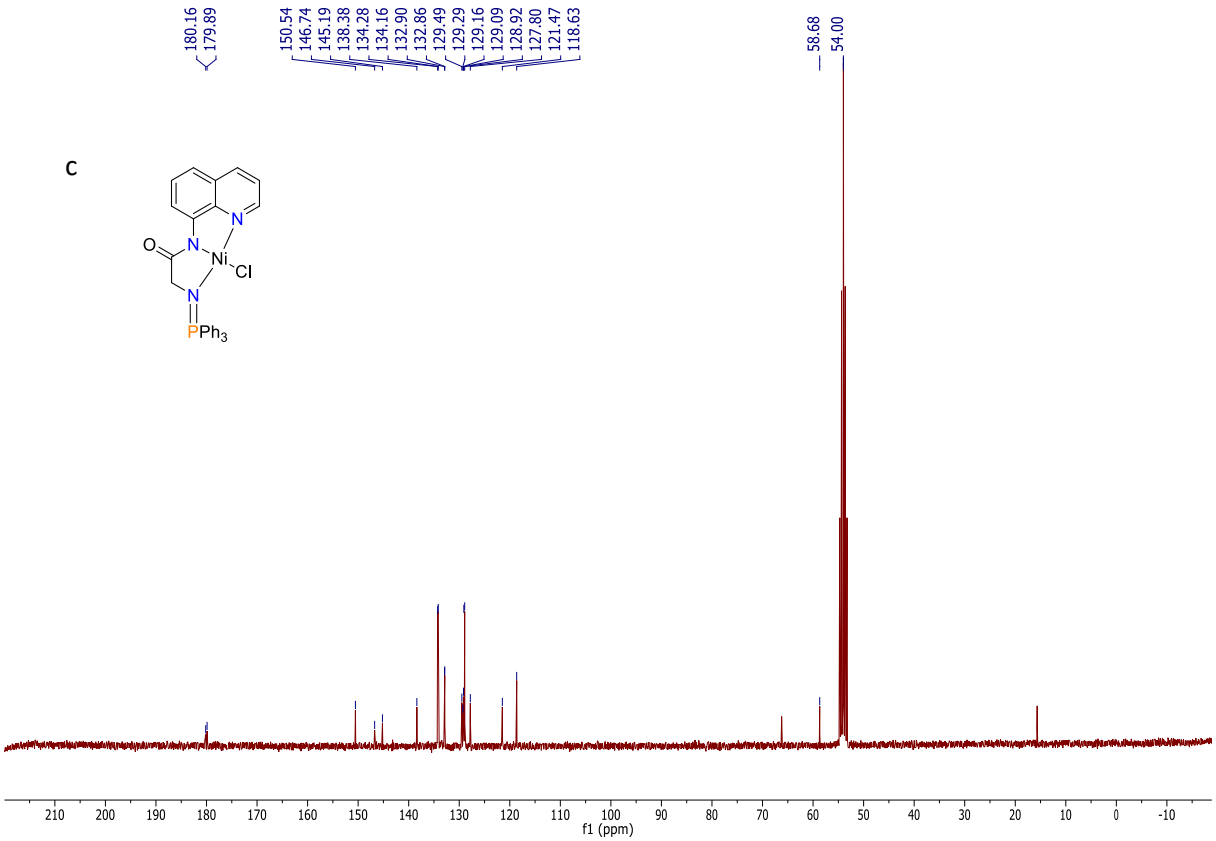
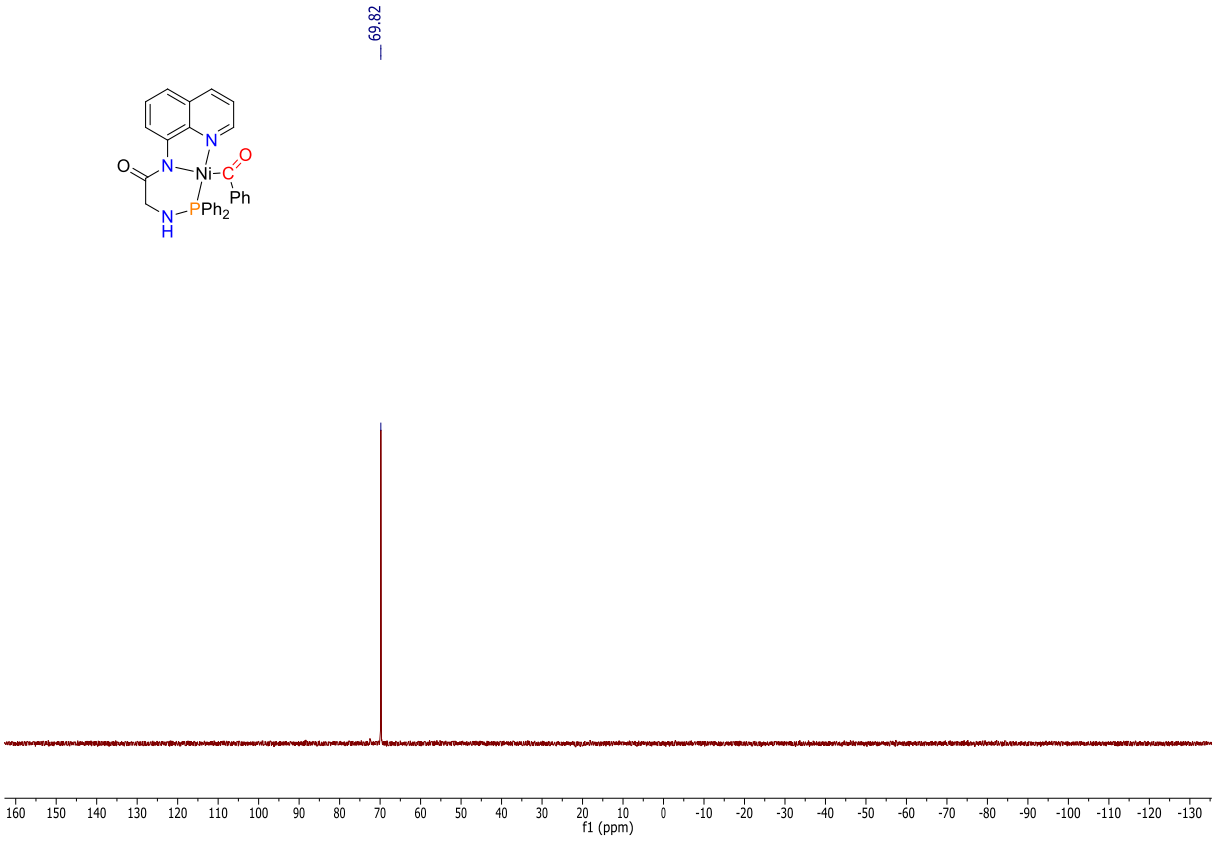


Figure S10. $^{31}P\{^{1}H\}$ (a), ^{1}H (b), ^{13}C (c) NMR spectra of **3**



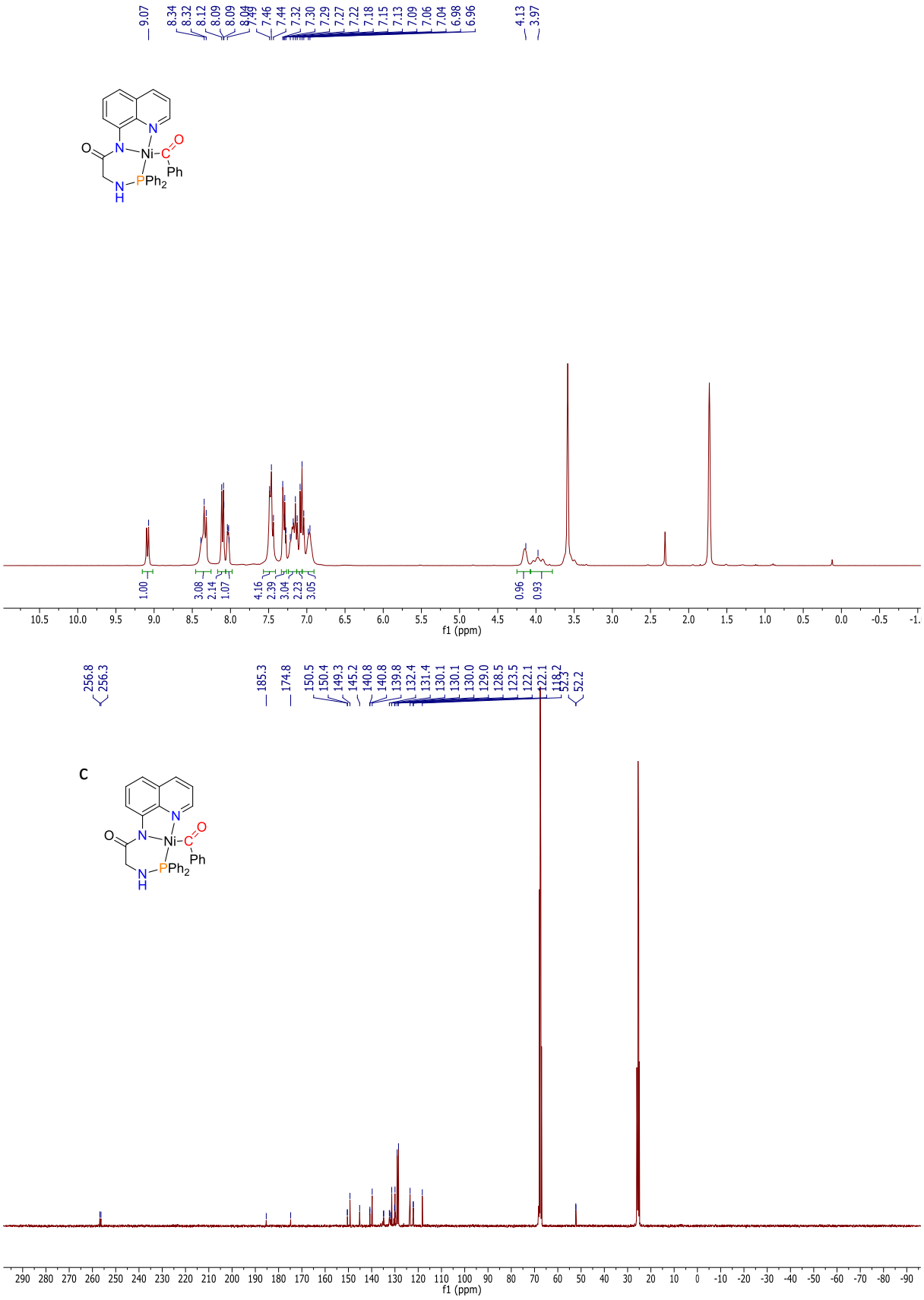


Figure S11. $^{31}P\{^{1}H\}$ (a), ^{1}H (b), ^{13}C (c) NMR spectra of **6**