Electronic Supplementary Material for Dalton Transactions

Supporting Information

Bis(isothiocyanato)bis(phosphine) complexes of group 10 metals: reactivity toward organic isocyanides

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Experimental

Data for $Ni(NCS)_2(CN–C_6H_3\text{-}2,6\text{-}Me_2)(PMe_2Ph)_2$, (1): ν_{max}/cm^{-1} 2136 (N≡C), 2072 (NCS); δ_H (300 MHz in $CDCl_3$): 1.90 (s, 12H, $P(CH_3)_2Ph$), 1.93 (s, 6H, CH_3), 6.96 (d, *J* = 7.9 Hz, Ph), 7.11–7.16 (m, 1H, Ph), 7.44–7.73 (m, 6H, Ph), 7.74–7.75 (m, 4H, Ph); δ_C ($CDCl_3$): 12.9 (s, $P(CH_3)_2Ph$), 18.4 (s, CH_3), 126.5, 128.0, 129.1, 129.7, 130.3, 131.1, 132.1 (s, NCS), 132.7, 135.1, 141.0 (S, Ph). The CNR carbon atom could not be assigned because of its low intensity. δ_P ($CDCl_3$) 11.0 (s).

Data for Ni(NCS)$_2$(CN–*t*-Bu)(PMe$_2$Ph)$_2$, (2): ν_{max}/cm^{-1} 2186 (N≡C), 2093, 2078 (NCS); δ_H (300 MHz in $CDCl_3$): 1.06 (s, 9H, C(C*H*$_3$)$_3$), 1.86 (s, 12H, P(C*H*$_3$)$_2$Ph), 7.50–7.54 (m, 6H, Ph), 7.79–7.83 (m, 4H, Ph).); δ_C ($CDCl_3$) 13.0 (br, P(*C*H$_3$)$_2$Ph), 29.6 (s, CH_3), 59.3 (s, *C*(CH$_3$)$_3$), 129.1, 130.5, 131.1, 132.7 (s, NCS), 139.5 (s, Ph); δ_P ($CDCl_3$) 14.4 (s).

Data for [Ni(P(*n*-Pr)$_3$)$_2$(CN–*t*-Bu)$_3$]$^{2+}$[Ni(1,3-μ-NCS)(NCS)$_3$]$_2^{2-}$, (3) ·(4): μ_{eff} = 2.71 μ_B. ν_{max}/cm^{-1} 2168 (N≡C), 2074 (NCS); δ_H (300 MHz in $CDCl_3$) 1.14 (t, *J* = 7.0 Hz, 18H, P(CH$_2$CH$_2$C*H*$_3$)$_3$), 1.60 (s, 27H, C(C*H*$_3$)$_3$), 1.64 (br, P(C*H*$_2$CH$_2$CH$_3$)$_3$), 1.92 (br, P(CH$_2$C*H*$_2$CH$_3$)$_3$); δ_P ($CDCl_3$) 24.9 (br).

Data for [Ni(P(*n*-Pr)$_3$)$_2$(CN–*t*-Bu)$_2$](SCN)$_2$: μ_{eff} = 0.98 μ_B. ν_{max}/cm^{-1} 2167 (N≡C), 2098, 2047 (NCS); δ_H (300 MHz in $CDCl_3$) 1.14 (t, *J* = 7.1 Hz, 18H, P(CH$_2$CH$_2$C*H*$_3$)$_3$), 1.57 (s, 18H, C(C*H*$_3$)$_3$), 1.68 (br, P(C*H*$_2$CH$_2$CH$_3$)$_3$), 1.82 (br, P(CH$_2$C*H*$_2$CH$_3$)$_3$); δ_P ($CDCl_3$) 24.1 (br).

Data for Pd(NCS)(SCN)(CN–*t*-Bu)(P(*n*-Pr)$_3$), (5): ν_{max}/cm^{-1} 2218 (N≡C), 2096, 2064 (NCS). δ_H (300 MHz in $CDCl_3$ at –60 °C) 1.14 (t, *J* = 7.0 Hz, 9H, P(CH$_2$CH$_2$C*H*$_3$)$_3$),

1.61 (br, 6H, P(C*H*$_2$CH$_2$CH$_3$)$_3$), 1.72 (s, 9H, C(C*H*$_3$)$_3$), 2.15 (br, 6H, P(CH$_2$C*H*$_2$CH$_3$)$_3$); δ_C ($CDCl_3$) 15.9 (d, *J* = 17 Hz, P(CH$_2$CH$_2$*C*H$_3$)$_3$, 16.8 (d, 137.7 Hz, P(*C*H$_2$CH$_2$CH$_3$)$_3$), 26.6 (br, P(CH$_2$*C*H$_2$CH$_3$)$_3$), 29.4 (s, C(*C*H$_3$)$_3$), 60.9 (s, *C*(CH$_3$)$_3$), 129.9 (s, NCS). The CNR carbon atom could not be assigned because of its too low intensity. δ_P ($CDCl_3$) 12.4 (s).

Data for {Pd(CN-*i*-Pr)$_2$[P(*n*-Pr)$_3$]$_2$}(SCN)$_2$ (6): ν_{max}/cm^{-1} 2224 (N≡C), 2096, 2052 (NCS); δ_H (300 MHz in $CDCl_3$) 1.13 (t, *J* = 7.1 Hz, 18H, P(CH$_2$CH$_2$C*H*$_3$)$_3$), 1.53 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.63 (m, 12H, P(C*H*$_2$CH$_2$CH$_3$)$_3$), 2.08 (m, 12H, P(CH$_2$C*H*$_2$CH$_3$)$_3$), 4.46 (sep, *J* = 6.6 Hz, C*H*(CH$_3$)$_3$); δ_C ($CDCl_3$) 15.8 (t, *J* = 7.2 Hz, P(CH$_2$*C*H$_2$CH$_3$)$_3$, 17.9 (s, P(*C*H$_2$CH$_2$*C*H$_3$)$_3$), 22.6 (s, CH(*C*H$_3$)$_2$), 26.6 (t, *J* = 14 Hz, P(*C*H$_2$CH$_2$CH$_3$)$_3$), 48.8 (s, *C*H(CH$_3$)$_2$), 132.5 (s, NCS). The CNR carbon atom could not be assigned because of its low intensity. δ_P ($CDCl_3$) 15.7 (s).

Data for [Pd(CN–*t*-Bu)$_2$(PMe$_3$)$_2$](SCN)$_2$ (7); ν_{max}/cm^{-1} 2227 (N≡C), 2047 (NCS); δ_H 1.56 (s, 18H, P(C*H*$_3$)$_3$), 1.75 (br , 18H, C(C*H*$_3$)$_3$); δ_C (DMSO-d_6) 14.9 (br, P(*C*H$_3$)$_3$), 28.9 (s, C(*C*H$_3$)$_3$), 60.3 (s, *C*(CH$_3$)$_3$); δ_P (DMSO-d_6): –7.31 (s).

Data for [Pd(CN–*t*-Bu)$_2$(PMePh$_2$)$_2$](SCN)$_2$ (8); ν_{max}/cm^{-1} 2229 (N≡C), 2068 (NCS); δ_H (300 MHz in $CDCl_3$) 0.97 (s, 18H, C(C*H*$_3$)), 2.56 (s, 6H, PC*H*$_3$Ph$_2$), 7.56–7.63 (m, 12H, Ph), 7.82–7.87 (m, 8H, Ph); δ_C ($CDCl_3$) 14.6 (br, P*C*H$_3$Ph$_2$), 29.2 (s, C(*C*H$_3$)$_3$), 59.5 (s, *C*(CH$_3$)$_3$), 129.2, 129.5, 130.7, 132.0, 132.4(s, Ph); δ_P ($CDCl_3$) 7.29 (s).

Data for [Pd(CN–*i*-Pr)$_2$(PMe$_3$)$_2$](SCN)$_2$ (9); ν_{max}/cm^{-1} 2229 (N≡C), 2054 (NCS); δ_H (300 MHz in $CDCl_3$) 1.57 (d, J = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.89 (s, 18H, P(C*H*$_3$)$_3$), 4.44 (sep, *J* = 6.6 Hz, C*H*(CH$_3$)$_2$); δ_C ($CDCl_3$) 16.0 (br, P(*C*H$_3$)$_3$), 22.5 (s, C(*C*H$_3$)$_2$), 50.4 (s, *C*(CH$_3$)$_2$), 129.9 (NCS); δ_P ($CDCl_3$) –9.12 (s).

Data for [Pd(CN–C$_6$H$_3$-2,6-Me$_2$)$_2$(PMePh$_2$)$_2$](SCN)$_2$ (10): ν_{max}/cm^{-1} 2189 (N≡C), 2070 (NCS); δ_H (300 MHz in $CDCl_3$) 2.12 (s, 12H, CH$_3$), 2.51 (s, 6H, PC*H*$_3$Ph$_2$), 6.99 (br, 4H, Ph), 7.13–7.18 (m, 2H, Ph), 7.39–7.43 (m, 12H, Ph), 7.73–7.76 (m, 8H, Ph); δ_C ($CDCl_3$) 13.5 (br, P*C*H$_3$Ph$_2$), 18.6 (s, CH$_3$), 125.5, 127.8, 129.1, 129.7, 131.0, 131.5, 132.5, 135.2 (s, Ph).); δ_P ($CDCl_3$) 10.7 (s).

Data for [Pt(CN-C$_6$H$_3$-2,6-Me$_2$)$_2$(PMe$_3$)$_2$](SCN)$_2$, (11); ν_{max}/cm^{-1} 2192 (N≡C), 2051 (NCS); δ_H (300 MHz in $CDCl_3$) 2.09 (t, *J* = 3.8 Hz, J_{PtH} = 27 Hz, 18H, P(C*H*$_3$)$_3$), 2.58 (s,

12 H, CH_3), 7.18–7.21 (m, 4H, Ph), 7.29–7.36 (m, 2H, Ph); δ_C ($CDCl_3$) 15.9 (t, J = 19 Hz, P(CH_3)$_3$), 19.1 (s, CH_3), 125.0, 128.6, 130.8 (s, NCS), 131.1, 136.2 (s, Ph).); δ_P ($CDCl_3$) –22.8 (s, J_{PtP} = 1996 Hz).

Data for [Pt(CN–C$_6$H$_3$-2,6-Me$_2$)$_2$(PEt$_3$)$_2$](SCN)$_2$, (12); ν_{max}/cm^{-1} 2189 (N≡C), 2071, 2052 (NCS); δ_H (300 MHz in $CDCl_3$) 1.26 (m, 18H, P(CH_2CH_3)$_3$), 2.27 (m, 12H, P(CH_2CH_3)$_3$), 2.51 (s, 12H, CH_3), 7.19–7.21 (m, 4H, Ph), 7.29–7.35 (m, 2H, Ph); δ_C ($CDCl_3$) 8.09 (s, P(CH_2CH_3)$_3$), 16.5 (t, J = 17 Hz, P(CH_2CH_3)$_3$), 18.9 (s, CH_3), 117.8, 128.5, 130.6 (br, NCS), 135.4 (s, Ph); δ_P ($CDCl_3$) 16.3 (s, J_{PtP} = 1974 Hz).

Data for [Pt(CN–C$_6$H$_3$-2,6-Me$_2$)$_2$(P(*n*-Pr)$_3$)$_2$](SCN)$_2$, (13): ν_{max}/cm^{-1} 2194 (N≡C), 2048 (NCS); δ_H (300 MHz in $CDCl_3$) 1.08 (t, J = 7.2 Hz, 18H, P($CH_2CH_2CH_3$)$_3$), 1.68 (m, 12H, P($CH_2CH_2CH_3$)$_3$), 2.18 (m, 12H, P($CH_2CH_2CH_3$)$_3$), 2.50 (s, 12H, CH_3), 7.18 (d, J = 7.7 Hz, 4H, Ph), 7.27–7.32 (m, 2H, Ph); δ_C ($CDCl_3$) 15.8 (t, J = 7.4 Hz, P($CH_2CH_2CH_3$)$_3$, 17.9 (s, J_{PtC} = 17 Hz, P($CH_2CH_2CH_3$)$_3$), 18.9 (s, CH_3), 26.1 (t, J = 16 Hz, P($CH_2CH_2CH_3$)$_3$), 116.9, 128.5, 130.2 (s, NCS), 135.2, 145.1 (s, Ph). The carbon atom of CNR could not be assigned due to its weak intensity. δ_P ($CDCl_3$) 9.14 (s, J_{PtP} = 1946 Hz).

Data for [Pd(CN–*i*-Pr)(SCN)(PEt_3)$_2$](SCN), (14): ν_{max}/cm^{-1} 2249 (N≡C), 2114, 2057 (NCS); δ_H (300 MHz in $CDCl_3$) 1.29 (q, *J* = 7.3 Hz, 18H, $P(CH_2CH_3)_3$), 1.57 (d, *J* = 6.6 Hz, 6H, $C(CH_3)_2$), 2.14 (m, 12H, $P(CH_2CH_3)_3$); δ_C ($CDCl_3$) 8.31 (s, $P(CH_2CH_3)_3$), 16.3 (br, $P(CH_2CH_3)_3$), 22.4 (s, $C(CH_3)_2$), 51.0 (s, $C(CH_3)_2$), 132.0 (br, NCS); δ_P ($CDCl_3$) 22.6 (s).

Data for [Pd(CN–C_6H_3-2,6-Me_2)(SCN)(PEt_3)$_2$](SCN), (15): ν_{max}/cm^{-1} 2196 (N≡C), 2106, 2056 (NCS); δ_H (300 MHz in $CDCl_3$) 1.26 (q, *J* = 7.3 Hz, 18H, $P(CH_2CH_3)_3$), 2.06 (br, 12H, $P(CH_2CH_3)_3$), 2.49 (s, 6H, CH_3), 7.13–7.16 (m, 2H, Ph), 7.23–7.28 (m, 1H, Ph); δ_C ($CDCl_3$) 8.18 (s, $P(CH_2CH_3)_3$), 15.5 (br, $P(CH_2CH_3)_3$), 19.0 (s, CH_3), 128.2, 129.6, 132.5 (br, NCS), 140.0 (s, Ph); δ_P ($CDCl_3$) 23.3 (s).

Data for [Pd(CN–C_6H_3-2,6-*i*-Pr_2)$_2$(PMe_3)$_2$](SCN)$_2$, (16): ν_{max}/cm^{-1} 2196 (N≡C), 2055 (NCS); δ_H (300 MHz in $CDCl_3$) 1.32 (d, *J* = 7.9 Hz, 24H, $CH(CH_3)_2$), 1.82 (s, 18 H, $P(CH_3)_3$), 3.40 (sep, *J* = 6.9 Hz, 4H, $CH(CH_3)_2$), 7.23 (d, *J* = 7.9 Hz, Ph), 7.44 (t, *J* = 7.9 Hz, 2H, Ph); δ_C ($CDCl_3$) 15.1 (br, $P(CH_3)_3$), 23.1 (s, $CH(CH_3)_2$), 30.0 (s, $CH(CH_3)_2$), 122.2, 123.9, 126.6, 130.0 (s, NCS), 145.8 (s, Ph); δ_P ($CDCl_3$) -6.59 (s).

Data for [Pt(CN–C_6H_3-2,6-*i*-Pr_2)$_2$(PMe_3)$_2$](SCN)$_2$, (17): ν_{max}/cm^{-1} 2195 (N≡C), 2059 (NCS); δ_H (300 MHz in $CDCl_3$) 1.34 (d, J = 6.8 Hz, 24H, CH(CH_3)$_2$), 1.82 (s, J_{PtH} = 23 Hz, 18 H, P(CH_3)$_3$), 3.43 (sep, J = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 7.28 (d, J = 7.8 Hz, Ph), 7.48 (t, J = 7.8 Hz, 2H, Ph); δ_C ($CDCl_3$) 15.8 (t, J = 19 Hz, P(CH$_3$)$_3$), 23.3 (s, CH(CH$_3$)$_2$), 29.9 (s, CH(CH$_3$)$_2$), 122.3, 124.1, 130.6 (s, NCS), 131.5, 146.3 (s, Ph); δ_P ($CDCl_3$) – 21.0 (s, J_{PtP} = 1960 Hz).

Data for Ni(CN–C_6H_3-2,6-*i*-Pr_2)(NCS)$_2$(PMe_3)$_2$, 18: ν_{max}/cm^{-1} 2163 (N≡C), 2102, 2047 (NCS); δ_H (300 MHz in $CDCl_3$) 1.31 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.56 (s, 18 H, P(CH_3)$_3$), 3.38 (sep, J = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 7.24 (d, J = 7.7 Hz, 2H, Ph), 7.42 (t, J = 7.9 Hz, 1H, Ph); δ_C ($CDCl_3$) 14.5 (t, J = 16 Hz, P(CH$_3$)$_3$), 23.3 (s, CH(CH$_3$)$_2$), 30.0 (s, CH(CH$_3$)$_2$), 123.0, 124.0, 130.5, 133.9 (s, NCS), 145.6 (s, Ph); δ_P ($CDCl_3$) 10.6 (s).

Data for Pt(NCS)$_2$(depe); ν_{max}/cm^{-1} 2125, 2098, 2056 (NCS): δ_H (300 MHz in DMSO-d_6) 1.20 (m, 12H, –P(CH$_2$CH_3)$_2$), 2.01–2.30 (m, 12 H, –P(CH_2CH$_3$)$_2$); δ_P (DMSO-d_6) 50.5 (bd, J = 142 Hz, J_{PtP} = 3377 Hz), 63.3 (s, J_{PtP} = 3076 Hz), 63.6 (s, J_{PtP} = 3034 Hz).

Data for $[Pt(depe)_2](SCN)_2$, (19):. IR (KBr, cm^{-1}): ν_{max}/cm^{-1} 2052 (NCS); δ_H (300 MHz in DMSO-d_6) 1.11 (m, 12H, $-P(CH_2CH_3)_2$), 2.10-2.50 (m, 12 H, $-P(CH_2CH_3)_2$); δ_P (DMSO-d_6) 58.3 (s, J_{PtP} = 2124 Hz).