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Synthesis and chemistry of bis(triisopropylphosphine) nickel(I) and nickel(0) precursors†

Robert Beck, Manar Shoshani, Jonathan Krasinkiewicz, Jillian A. Hatnean and Samuel A. Johnson*

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High yield syntheses of $(^{i}Pr_3P)_2NiX$ (**3a–c**), (where X = Cl, Br, I) were established by comproportionation of $(^{i}Pr_3P)_2NiX_2$ (**1a–c**) with $(^{i}Pr_3P)_2Ni(\eta^2\text{-}C_2H_4)$ (**2**). Reaction of **1a** with either NaH or $LiHBEt_3$ provided $(^{i}Pr_3P)_2NiHCl$ (**4**), along with **3a** as a side-product. Reduction of $(^{i}Pr_3P)_2NiCl$ (**3a–c**) with Mg in presence of nitrogen saturated THF solutions provided the dinitrogen complex $[(^{i}Pr_3P)_2Ni]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**5**). In aromatic solvents such as benzene and toluene a thermal equilibrium exists between **5** and the previously reported monophosphine solvent adducts $(^{i}Pr_3P)Ni(\eta^6\text{-arene})$ (**6a,b**). Reaction of **5** with carbon dioxide provided $(^{i}Pr_3P)_2Ni(\eta^2\text{-}CO_2)$ (**7**). Thermolysis of **9** at 60 °C provided a mixture of products that included the reduction product $(^{i}Pr_3P)_2Ni(CO)_2$ (**8**) along with $^{i}Pr_3P{=}O$, as identified by NMR spectroscopy. Complex **8** was also prepared in high yield from the reaction of **5** with CO. Reaction of **5** with CS_2 gave the dimeric carbon disulfide complex $[(^{i}Pr_3P)Ni(\mu\text{-}\eta^1{:}\eta^2\text{-}CS_2)]_2$ (**9**). Diphenylphosphine reacts with **5** to form the dinuclear Ni(I) complex $[(^{i}Pr_3P)Ni(\mu_2\text{-}PPh_2)]_2$ (**10**). Complex **5** reacts with PhSH to form $(^{i}Pr_3P)_2Ni(SPh)(H)$ (**11**), which slowly loses H_2 and $^{i}Pr_3P$ to form the dimeric Ni(I) complex $[(^{i}Pr_3P)Ni(\mu_2\text{-}SPh)]_2$ (**12**) at room temperature. Complex **12** was also accessed by salt metathesis from the reaction of $(^{i}Pr_3P)_2NiCl$ (**3a**) with PhSLi, which demonstrates the utility of **3a** as a Ni(I) precursor. With the exception of **6a,b**, all compounds were structurally characterized by single-crystal X-ray crystallography.

Introduction

Over the past decade increased efforts have been made to expand the utility of Ni in catalysis, driven by its greater availability and lower cost compared precious metal catalysts. Complexes of Ni are capable of a variety of cross-coupling reactions,[1] as well as the activation of traditionally inert C–H, C–F, and C–O bonds.[2] These inert bond activation reactions include catalytic transformations[2a] such as the unprecedented stannylation of C–H bonds,[3] coupling reactions with C–F bonds,[2a,4] and C–O bond hydrogenation and coupling reactions.[2b,e,f,5] Phosphine supported complexes of low-valent nickel complexes play a role as catalysts or intermediates in many of these reactions.

Our research has probed the use of phosphine supported Ni(0) synthons, such as the anthracene complex $(^{i}Pr_3P)_2Ni(\eta^2\text{-}C_{14}H_{10})$, in the isolation of Ni(0) intermediates in reactions that include C–H, C–F and C–C bond activation.[2a,3,6] Surprisingly few fully-characterized complexes of the readily available bulky phosphine donor $^{i}Pr_3P$ have been reported; for example, a search of the CSD[7] for the $(^{i}Pr_3P)_2Ni$ fragment provided 6 entries, 4 of which we have published in the last 2 years. We have found that bulky Ni(0) precursors can change the course of reactivity, and that the chemistry of the $^{i}Pr_3P$ ligand is often significantly different from that of slightly less bulky phosphines such as Et_3P,[6b] and allows the isolation of unexpected reaction intermediates.[8] Reactions of $(^{i}Pr_3P)_2Ni(0)$ precursors also appear prone to loss of $^{i}Pr_3P$ and the formation of complexes containing either the $(^{i}Pr_3P)Ni(0)$ or $(^{i}Pr_3P)Ni(I)$ moiety.[6e] Unlike the coordination chemistry of nickel centers in the 0 and +2 and oxidation state, the chemistry of Ni(I) complexes is less well developed. Mononuclear complexes of the type $(Ph_3P)_2NiX$[9] and related systems with tri-alkyl, aryl or bis-chelating-phosphines have been described[10] as reactive intermediates of redox reactions *via* EPR-spectroscopy or electrochemically.[11] Despite the synthetic potential of such precursors, high-yield synthetic routes to $(R_3P)_2NiX$ species, where R is a large electron-donating substituent such as ^{i}Pr, are not well-known.

Herein, we report the high yield syntheses of the Ni(I) precursors $(R_3P)_2NiX$ (X = Cl, Br, I) and the Ni(0) precursor $[(^{i}Pr_3P)_2Ni]_2(\mu\text{-}N_2)$ (**5**), along with some reactions showing their synthetic utility in the preparation of Ni(0), Ni(I) and Ni(II) complexes.

Department of Chemistry and Biochemistry, University of Windsor, Sunset Avenue 401, Windsor, ON N9B 3P4, Canada. E-mail: sjohnson@uwindsor.ca; Fax: (+1) 519-973-7098

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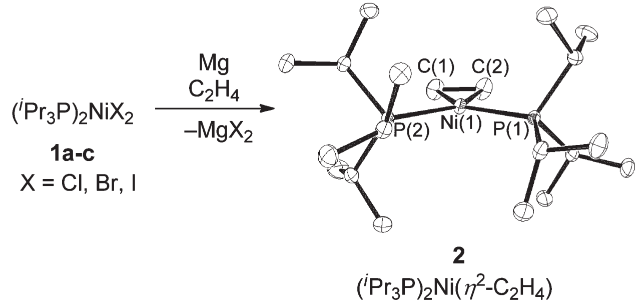
Preparation and characterization of $(^{i}Pr_3P)_2NiX_2$ (X = Cl, Br, I) (1a–c)

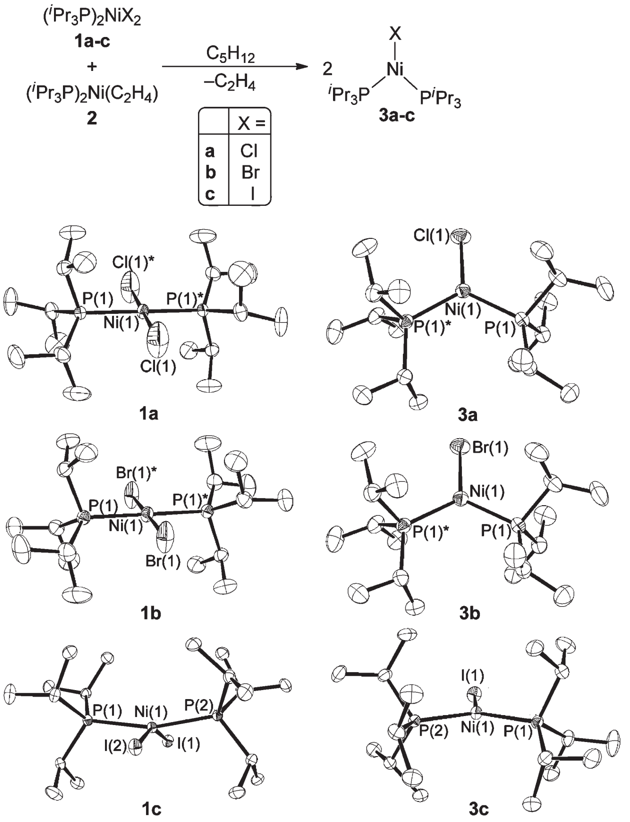
Heterogeneous mixtures of powdered, anhydrous NiX_2 (X = Cl, Br, I) react within a period of 3 d in toluene in the presence of two equivalents $^{i}Pr_3P$ to provide $(^{i}Pr_3P)_2NiX_2$ (**1a–c**) as analytically pure dark red rhombic crystals in almost quantitative yields (94–97%). Complexes **1a–c** are far less soluble in toluene (2 g per 150 mL), when compared to the triethylphosphine congeners $(PEt_3)_2NiX_2$. Syntheses of complexes **1a** and **1b** have been reported previously;[12] however, the reported syntheses in EtOH provided lower yields.[12b] Full characterization is lacking in the literature even for the previously reported compounds. The ^{1}H and $^{13}C\{1H\}$ NMR spectra of **1a–c** are nearly identical. The coordinated $^{i}Pr_3P$ ligands in **1a–c** show two sets of ^{1}H resonances with a doublet for the methyl substituents at $\delta \sim 1.2$ and a septet at $\delta \sim 2.2$ for the C–H group of $^{i}Pr_3P$ ligand. The $^{13}C\{^{1}H\}$ NMR spectra feature a singlet at δ 20.2 and a broad singlet at δ 23.1. Complexes **1a–c** do not have an observable $^{31}P\{^{1}H\}$ NMR signal at room temperature, consistent with the failure to observe coupling to ^{31}P in both the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. This suggests rapid relaxation of the ^{31}P nuclear spin by a contact mechanism from a thermally accessible electronic triplet spin state. Under some conditions $^{31}P\{^{1}H\}$ NMR spectra of solutions of **1a–c** provide singlets, with chemical shifts (**1a**, δ 21.0; **1b**, δ 22.0; **1c**, δ 24) that are suggestive of dissociation of free $^{i}Pr_3P$ (δ 20.5). Dilute samples of **1b** and **1c** dissolve with a green color, also suggestive of complicated solution behavior. Efforts to prepare $(^{i}Pr_3P)_2NiF_2$ from NiF_2 using similar reaction conditions failed, despite precedent for closely related reactions.[13]

The molecular structures of **1a–c** were characterized by single-crystal X-ray diffraction techniques, and for **1a** and **1b** feature the expected square planar coordination geometries. A lower-quality disordered room-temperature structure of **1b** has been obtained previously.[14] The iodo derivative **1c** has a slight distortion away from square planar towards tetrahedral, as shown in Scheme 1. The distortion is presumably due to the steric requirements of the bulky $^{i}Pr_3P$ and iodo ligands. The bond angles I(1)–Ni(1)–I(2) and P(2)–Ni(1)–P(1) deviate from linearity by 26° and 17°, respectively. A summary of bond lengths is provided in Table 1.

It has been previously shown that $(^{i}Pr_3P)_2Ni(\eta^2\text{-}C_2H_4)$ (**2**) can be prepared in moderate yield from the reaction of $Ni(C_2H_4)_3$ with $^{i}Pr_3P$.[15] A more convenient synthesis is the reaction of **1a–c** with magnesium in the presence of ethylene, as shown in eqn (1). The reaction afforded yellow crystals of the $16e^{-}$ complex **2** in 83% yield.



(1)



Scheme 1 Syntheses of Ni(I) reagents **3a–c** from **1a–c** and **2** and ORTEPs of their solid-state structures with 30% probability ellipsoids.

Complex **2** is very soluble in *n*-pentane and concentrated solutions at −34 °C afforded single crystals suitable for X-ray crystallography. The structure is typical for Ni(0) bis(phosphine) adducts. The C(1)–C(2) bond length of 1.386(3) Å for the π-coordinated ethylene is slightly elongated when compared to free ethylene (1.340 Å)[16] and closely related with the structural parameters of the related literature complexes $(dtbpe)Ni(\eta^2\text{-}C_2H_4)$[17] [dtbpe = 1,2-bis-(di-*tert*-butyl-phosphino)-ethane] and $(PPh_3)_2Ni(\eta^2\text{-}C_2H_4)$.[18]

Preparation and characterization of $(^{i}Pr_3P)_2NiX$ (X = Cl, Br, I) (3a–c)

Solutions of $(^{i}Pr_3P)_2NiX_2$ (**1a–c**) with a slight excess of $(^{i}Pr_3P)_2Ni(\eta^2\text{-}C_2H_4)$ (**2**) in *n*-pentane undergo comproportionation to afford $(^{i}Pr_3P)_2NiX$ (3 h for **3a**, 30 min for **3b**, 5 min **3c**), as shown in Scheme 1. A similar approach was reported for PPh_3 supported Ni complexes.[19] The progress of the reaction can be visually monitored by the slow dissolution of the sparingly soluble $(^{i}Pr_3P)_2NiX_2$ (**1a–c**) in *n*-pentane. Complexes **3a–c** were easily isolated by removal of the volatiles under vacuum and washing the residue with ice cold *n*-pentane to remove the slight excess of **2**.

The effective magnetic moments (μ_{eff}) of **3a–c** were determined using Evans method to be in the range of 2.05–2.19 μ_B, which is in agreement for other d^9 nickel complexes with one

Table 1 Selected bond lengths [Å] and angles [°] of basic *mono-* and *di*-halogeno bisphosphine nickel complexes **1a–c** and **3a–c**

	1a	**1b**	**1c**	**3a**	**3b**	**3c**	**4**
Ni–X [Å]	2.193(2)	2.3195(5)	2.5102(7)	2.1761(7)	2.3033(7)	2.4810(7)	2.2062(7)
Ni–P [Å]	2.2572(11)	2.2898(10)	2.3098(13) 2.2896(12)	2.2215(5)	2.2230(7)	2.2336(10) 2.2402(10)	2.1845(7) 2.1858(7)
P–Ni–P [°]	180.0	180.0	163.71(5)	119.44(2)	120.18(3)	126.05(4)	163.10(2)
X–Ni–X [°]	180.0	180.0	154.24(3)	—	—	—	178.8(12)
P–Ni–X [°]	89.55(6)	90.63(3)	92.18(4) 92.29(4)	120.282(12)	119.911(17)	119.02(3) 114.93(3)	98.21(3) 98.64(3)

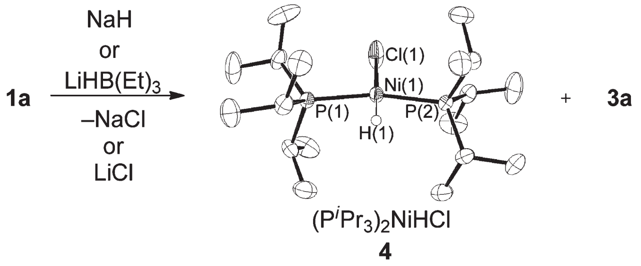
unpaired electron.[10b,20] The ^{1}H NMR spectra of paramagnetic **3a–c**, show broad paramagnetically shifted resonances for the methyl groups of the ^{i}Pr$_3$P moieties in the range of δ 3.1–3.3, and the methine C–H at δ 50–60. Although the EPR spectra and reactivity of complexes **3a** and **3b** have been previously reported,[21] high-yield syntheses and complete characterizations have not.

Complexes **3a–c** are stable in the solid state for months at −34 °C without any signs of decomposition. Solutions of **3a–c** in aromatic solvents such as toluene and benzene start to decompose within a period of 24 h by disproportionation, which yields (^{i}Pr$_3$P)$_2$NiX$_2$ (**1a–c**) and a nickel mirror, but *n*-pentane solutions of **3a–c** are significantly more stable. Single crystals of **3a–c** suitable for structural analysis were obtained by cooling concentrated *n*-pentane solutions to −34 °C. Depictions of the solid-state molecular structures are shown in Scheme 1, and X-ray crystallographic bond lengths and angles are provided in Table 1.

Complexes **3a–c** feature trigonal planar geometries around the nickel atom, with sums of X–Ni–P and P–Ni–P angles that are within 1° of 360°. The Ni–X and Ni–P bonds are all shorter in **3a–c** than in the related Ni(II) complexes **1a–c**, which may be attributable to decreased steric bulk about the three-coordinate *vs.* four-coordinate metal centres, rather than reflective of the relative sizes of Ni(I) *versus* Ni(II). A striking structural feature is the similar P–Ni–P angles in the chloro and bromo derivative **3a–b** of 119.44(2)° and 120.18(3)°, but the significantly larger P–Ni–P angle of 126.05(4)° in the iodo derivative. This complex also features dissimilar P–Ni–I bond angles of 119.02(3) and 114.93(3)°. A slight rotation of one of the ^{i}Pr$_3$P moieties in **3c** may occur to accommodate the larger iodo ligand, and this may account for the increase in P–Ni–P angle.

Structural characterization of (^{i}Pr$_3$P)$_2$NiHCl (4)

Attempts to generate **3a** directly from **1a** using alternate reducing agents failed to provide improved yields compared to the reaction of **1a** with **2**. For example, the reaction of **1a** with a slight excess of sodium hydride or LiHBEt$_3$ in THF provided a mixture of the known[12b,22] complex *trans*-(^{i}Pr$_3$P)$_2$NiClH (**4**) with **3a** as a significant byproduct. Complex **4** was readily isolated by removal of solvent under vacuum, extraction with cold *n*-pentane, removal of the less soluble alkali metal chlorides and the Ni(I) byproduct (**3a**) by filtration, and crystallization at −34 °C.

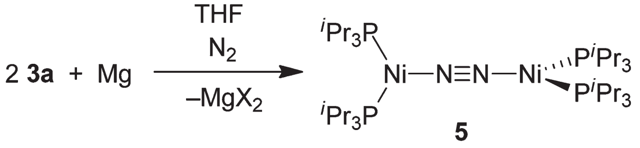


(2)

The solid-state structure of **4** has not been reported, and we were interested in how the structural parameters of **3a** might differ from **4**, to ensure that these species could be easily distinguished by crystallography. A comparison of the bond lengths and angles of **1a–c**, **3a–c** and **4**, are given in Table 1. The presence of a hydride ligand in **4** is obvious from the P(1)–Ni(1)–P(2) angle of 163.10(2)°, which is smaller than the 180° angle in **1a** and larger than the 119.44(2) angle in **3a**. The phosphine donors in **4** are bent away from the larger *chloro*-ligand. The electron density associated with the hydride ligand was located in difference Fourier map and lies with a Ni(1)–H(1) distance of 1.25(3) Å, though this short distances must be considered suspect in the absence of neutron diffraction data, particularly when compared with typical literature terminal Ni–H distances.[7,23a–c,e]

Synthesis and characterization of dinuclear dinitrogen complex (5)

The reduction of (^{i}Pr$_3$P)$_2$NiCl (**3a**) with an excess of magnesium in THF afforded the red complex [(^{i}Pr$_3$P)$_2$Ni]$_2$(μ-N$_2$) (**5**) in 78–85% yield, as shown in eqn (3). Dinitrogen complex **5** is extremely soluble in *n*-pentane, and after extensive drying under vacuum left a dark red waxy solid. Both the ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of THF solutions of (^{i}Pr$_3$P)$_2$NiCl (**3a**) under the reducing conditions used to prepare **5** provided no evidence for Ni(0) complexes with more than two ^{i}Pr$_3$P ligands, examples of which are known for the smaller phosphine ligands such as PEt$_3$.[24] This might be expected, given the large 160° Tolman cone angle for ^{i}Pr$_3$P,[25] which should prevent the formation of complexes such as (^{i}Pr$_3$P)$_3$Ni, though the complex (Cy$_3$P)$_3$Ni has been reported and used in synthesis[26] despite the similar phosphine cone angle of Cy$_3$P. Full structural characterization of (Cy$_3$P)$_3$Ni has not been reported. Solid **5** can be handled at 20 °C for weeks without significant decomposition, but gradually decomposes in polar organic solvents such as THF. The ^{31}P{^{1}H} NMR signal of **5** was observed at δ 43.7. Dinitrogen incorporation is confirmed by the broad singlet at δ −71.2, in the $^{15}N\{^1H\}$ NMR spectrum of $^{15}N_2$ labeled **5**, which is only modestly shifted relative to the chemical shift of free N_2. Due to the symmetry of complex **5**, no absorption band was observed in the IR spectrum in the range typical of dinitrogen complexes of 3rd row transition metals.[27] Both pentane solutions of **5** and solid **5** had strong Raman active stretches at 1908 cm^{-1}. The related dinuclear dinitrogen complex $[(Cy_3P)_2Ni]_2(\mu\text{-}N_2)$ has an IR active N–N stretching frequency at 2028 cm^{-1},[26c] which was suggested to be mononuclear species $(Cy_3P)_2Ni(\eta^1\text{-}N_2)$ from dissociation of a $(Cy_3P)_2Ni$ moiety from the dinuclear species in toluene.[26a] Supporting this assignment, a related structurally characterized mononuclear dinitrogen complex has been reported with an IR stretch at 2072 cm^{-1}.[28] Given the similar cone angles of Cy_3P and $^iPr_3P$, it is not clear why $[(Cy_3P)_2Ni]_2(\mu\text{-}N_2)$ provides $(Cy_3P)_2Ni(\eta^1\text{-}N_2)$ in solution whereas there is no sign that **5** converts to $(^iPr_3P)_2Ni(\eta^1\text{-}N_2)$ under similar conditions. It may be that stronger backdonation is occurring from the $(^iPr_3P)_2Ni$ moiety, as this factor often favors dinuclear bridging modes.[29] The reduction of $(^iPr_3P)_2NiX_2$ (**1a**) by Mg in THF under a N_2 atmosphere also provides **5**, as monitored by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. This is a useful *in situ* preparation of **5**; however, the product generated in this manner is reluctant to crystallize from either pentane or hexamethyldisiloxane.



(3)

Recrystallization of saturated solutions of **5** in hexamethyldisiloxane at −34 °C afforded red crystals of **5** in form of plates that were suitable for structural analysis. Repeated recrystallizations provided crystals that index as orthorhombic, but do not provide a reasonable structure solution in this crystal system. A solution based on a twinned monoclinic cell was determined for a partially twinned crystal. Due to the combination of disorder of some of the $^iPr_3P$ substituents and twinning, the structure is of somewhat low quality, but the N(1)–N(2) distance of 1.158(5) Å is reasonable for a weakly activated dinitrogen complex. A depiction of the solid-state molecular structure is shown in Fig. 1, and X-ray crystallographic collection and refinement parameters are included in Table 2.

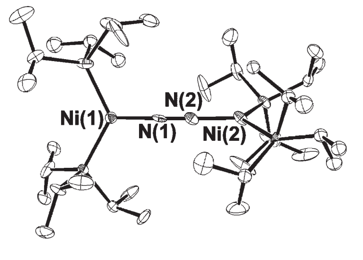


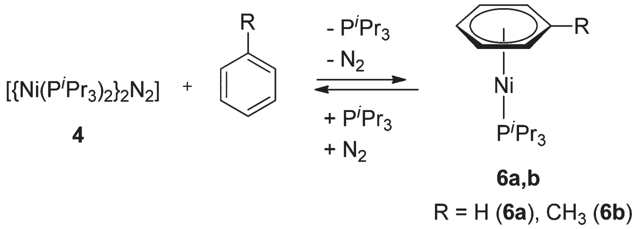
Fig. 1 ORTEP of **5** as determined by X-ray crystallography. Disordered fragments are excluded. Hydrogen atoms are omitted for clarity.

The core of the molecular structure of **5** has approximate D_2 symmetry, approaching an approximate D_{2d}, or allene-like structure. The plane containing the atoms Ni(1), P(1) and P(2) are almost perpendicular to the second plane consisting of Ni(2), P(3) and P(4), with an angle between planes of 81.05°. This near perpendicular arrangement presumably provides the closest approach of the two nickel fragments (~4.7 Å) to bind end-on with dinitrogen, as well as near optimal overlap with the orthogonal π^* orbitals on the N_2 moiety.

Complex 5 as a source of $(^iPr_3P)_2Ni$ and $(^iPr_3P)Ni$

We have been interested in bond activation reactions that utilize sources of the $(^iPr_3P)_2Ni$ or $(^iPr_3P)Ni$ moiety.[3,6c,e,8] The anthracene complex $[(^iPr_3P)_2Ni]_2(\eta^2\text{-}C_{14}H_{10})$ is a capable source,[6c] but has the downside of producing anthracene as a byproduct, which can be tedious to separate from products with similar solubilities. Complex **5** is a more versatile source, in that N_2 is readily removed from the reaction mixture.

Complex **5** undergoes an equilibrium reaction with benzene under an N_2 atmosphere. When **5** was dissolved in benzene at room temperature an additional singlet peak appeared at δ 58 in the $^{31}P\{^1H\}$ NMR spectrum together with a peak for *free* $^iPr_3P$ at δ 20.5. Similar observations were made for toluene (δ 59.0), which supports a thermal equilibrium between **5** and a solvent adduct **6a,b**, as shown in eqn (4). In contrast $[(Cy_3P)_2Ni]_2(\mu\text{-}N_2)$ was reported to convert to $(Cy_3P)_3Ni$ and $(Cy_3P)Ni$;[26a] the identity of the latter compound may be worth reinvestigation.



(4)

As monitored by variable-temperature NMR spectroscopy, more dinitrogen complex was present at low temperature, as expected for an equilibrium reaction. Attempts to trap the $^iPr_3P$ byproduct that prevented the isolation of **6a,b** with $Ni(COD)_2$ or Lewis acids were unsuccessful or led to unknown side products, thus **6a,b** were not isolated. Structurally related examples of related $Ni(\eta^6\text{-arene})$ complexes stabilized by phosphine, *N*-heterocyclic carbenes or silylene ligands have been reported.[30] The NMR data of the solvent adducts **6a,b** are identical with previous observations of a solvent dependent equilibrium with the anthracene adduct $(^iPr_3P)_2Ni(\eta^2\text{-}C_{10}H_{14})$ in aromatic solvents.[6c] Such reactivity suggests that in systems where a single phosphine provides stability, the steric bulk of the $^iPr_3P$ ligand provides an impetus for dissociation. The chemistry of these precursors can thus be expected to be different from the more thoroughly studied chelating bis(phosphine)Ni(0) precursors.[28,31]

Table 2 Data and structure refinement parameters for complexes **1–13**

	1a	**1b**	**1c**	**2**
Empirical formula	$C_{18}H_{42}P_2Cl_2Ni$	$C_{18}H_{42}Br_2NiP_2$	$C_{18}H_{42}P_2NiI_2$	$C_{20}H_{46}NiP_2$
F_w	450.07	538.99	632.97	407.22
Cryst syst	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a [Å]	8.2383(16)	8.1476(5)	15.249(3)	11.7420(3)
b[Å]	8.8394(18)	8.9382(6)	12.623(3)	13.3060(4)
c [Å]	16.113(3)	16.3133(10)	25.316(5)	16.8905(3)
α [°]	90	90	90	90
β [°]	93.70(3)	93.7970(10)	90	116.221(2)
γ [°]	90	90	90	90
V [Å^3]	1170.9(4)	1185.41(13)	4873.3(17)	2367.40(10)
Space group	$P21/c$	$P21/c$	$Pbca$	$P21/c$
Z value	2	2	8	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.277	1.510	1.725	1.143
μ (Mo-Kα) [mm^{-1}]	1.192	4.323	3.461	0.954
Temperature [K]	173(2)	173(2)	173(2)	173(2)
$2\Theta_{\max}$ [°]	50	51	52.7	53.4
Total no. of reflns.	10 964	11 551	49 168	25 356
No. unique data reflns; R_{int}	2076; 0.0304	2240; 0.0246	4972; 0.0749	5017; 0.0202
Abs cor	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Transmn factors	0.76–0.64	0.62–0.47	0.60–0.37	0.89–0.79
No of variables	112	112	220	236
Reflns/params	18.5	20.0	22.6	21.2
GOF on F^2	1.081	1.068	1.041	1.069
R_1; wR_2 ($I \geq 2\sigma$)	0.0571; 0.1611	0.0478; 0.1285	0.0347; 0.0678	0.0274; 0.0729
R_1; wR_2 (all data)	0.0623; 0.1673	0.0540; 0.13417	0.0518; 0.0749	0.0299; 0.0751
Residual density (e–/Å^3)	0.848; −1.446	1.529; −1.371	0.882; −0.455	0.503; −0.306

	3a	**3b**	**3c**	**4**
Empirical formula	$C_{18}H_{42}ClNiP_2$	$C_{18}H_{42}BrNiP_2$	$C_{18}H_{42}INiP_2$	$C_{18}H_{43}ClNiP_2$
F_w	414.62	459.08	506.07	415.62
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a [Å]	11.620(2)	11.714(2)	11.741(2)	16.264(3)
b [Å]	13.030(3)	13.115(3)	13.153(3)	8.9520(18)
c [Å]	15.806(3)	15.899(3)	17.089(6)	15.834(3)
α [°]	90	90	90	90
β [°]	106.85(3)	106.94(3)	114.76(2)	93.85(3)
γ [°]	90	90	90	90
V [Å^3]	2290.4(8)	2336.6(8)	2396.4(11)	2300.2(8)
Space group	$C2/c$	$C2/c$	$P21/c$	$P21/c$
Z value	4	4	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.202	1.305	1.403	1.200
μ (Mo-Kα) [mm^{-1}]	1.100	2.675	2.229	1.096
Temperature [K]	173(2)	173(2)	173(2)	173(2)
$2\Theta_{\max}$ [°]	52.04	52	51	52.1
Total no. of reflns.	11 590	11 892	23 211	23 069
No. unique data reflns; R_{int}	2253; 0.0155	2307; 0.0238	4480; 0.0255	4517; 0.0334
Abs cor	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Transmn factors	0.82–0.78	0.96–0.75	0.79–0.50	0.80–0.65
No of variables	107	107	211	115
Reflns/params	21.1	21.5	21.2	23.1
GOF on F^2	1.072	1.117	1.049	1.060
R_1; wR_2 ($I \geq 2\sigma$)	0.0224; 0.0612	0.0270; 0.0738	0.0357; 0.0827	0.0337; 0.0807
R_1; wR_2 (all data)	0.0230; 0.0621	0.0315; 0.0772	0.0408; 0.0865	0.0391; 0.0859
Residual density (e–/Å^3)	0.274; −0.233	0.590; −0.258	1.321; −0.496	0.778; −0.631

	5	**7**	**8**	**9**
Empirical formula	$C_{36}H_{84}N_2$ Ni_2P_2	$C_{19}H_{42}NiO_2P_2$	$C_{20}H_{42}Ni$ O_2P_2	$C_{20}H_{42}Ni_2P_2S_4$
F_w	786.35	423.18	435.19	590.14
Cryst syst	Monoclinic	Triclinic	Monoclinic	Triclinic
a [Å]	14.950(4)	8.1143(3)	11.660(2)	7.6433(15)
b [Å]	21.071(5)	8.4650(4)	14.224(3)	11.110(2)
c [Å]	15.531(4)	18.9139(3)	15.172(3)	17.163(3)
α [°]	90	89.3380(10)	90	87.22(3)
β [°]	114.158(5)	77.635(2)	111.17(3)	79.83(3)
γ [°]	90	64.2520(10)	90	71.63(2)
V [Å^3]	4464(2)	1138.11(7)	2346.4(8)	1361.5(5)

Table 2 *(Contd.)*

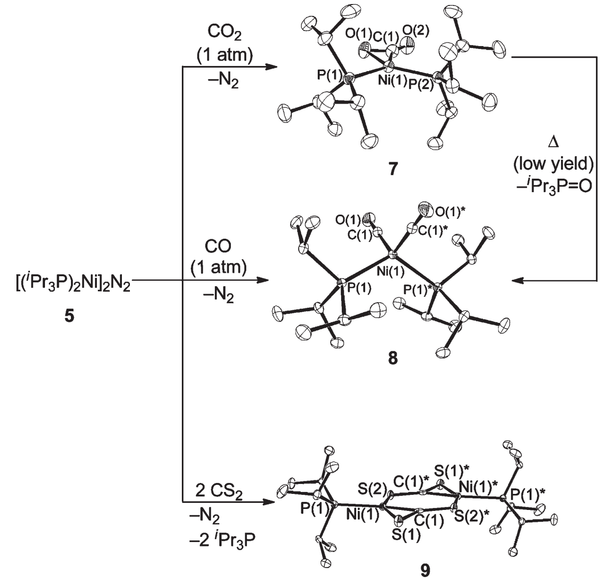
	5	**7**	**8**	**9**
Space group	$P2(1)/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
Z value	4	2	4	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.17	1.235	1.232	1.440
μ (Mo-Kα) [mm^{-1}]	1.011	1.002	0.974	1.813
Temperature [K]	173(2)	173(2)	173(2)	173(2)
$2\Theta_{\max}$ [°]	50.0	52.7	52.7	50
Total no. of reflns.	34 028	11 781	12 374	13 248
No. unique data reflns; R_{int}	Twinned	4610; 0.0341	2404; 0.0401	4779; 0.0863
Abs cor	None	Multi-scan	Multi-scan	Multi-scan
Transmn factors	—	0.78–0.66	0.95–0.79	0.93–0.65
No of variables	426	229	120	265
Reflns/params	—	20.1	20.0	18.0
GOF on F^2	1.244	1.217	1.085	0.981
R_1; wR_2 ($I \geq 2\sigma$)	0.094; 0.177	0.0488; 0.0930	0.0324; 0.0749	0.0579; 0.0934
R_1; wR_2 (all data)	0.138; 0.192	0.0600; 0.0996	0.0383; 0.0776	0.0999; 0.1091
Residual density (e−/Å^3)	1.276; −1.775	0.452; −0.277	0.405; −0.232	0.590; −0.478

	10	**11**	**12**
Empirical formula	$C_{42}H_{62}Ni_2P_4$	$C_{24}H_{48}P_2SNi$	$C_{20}H_{42}P_2S_4Ni_2$
F_w	808.22	489.33	590.14
Cryst syst	Monoclinic	Triclinic	Triclinic
a [Å]	10.8561(5)	9.1831(18)	7.6433(15)
b [Å]	17.7577(3)	11.038(2)	11.110(2)
c [Å]	11.3609(7)	13.734(3)	17.163(3)
α [°]	90	81.49(2)	87.22(3)
β [°]	107.813(3)	88.23(3)	79.83(3)
γ [°]	90	84.88(3)	71.63(2)
V [Å^3]	2085.15(16)	1371.1(5)	1361.5(5)
Space group	$P21/c$	$P\bar{1}$	$P\bar{1}$
Z value	2	2	2
$D_{\text{calcd.}}$ [g cm^{-3}]	1.287	1.185	1.440
μ (Mo-Kα) [mm^{-1}]	1.084	0.908	1.813
Temperature [K]	173(2)	173(2)	173(2)
$2\Theta_{\max}$ [°]	51.3	52.04	50
Total no. of reflns.	20 752	14 382	13 248
No. unique data reflns; R_{int}	3959; 0.0221	5385; 0.0347	4779; 0.0863
Abs cor	Multi-scan	Multi-scan	Multi-scan
Transmn factors	0.94–0.64	0.80–0.65	0.93–0.65
No of variables	223	269	265
Reflns/params	17.8	20.0	18.0
GOF on F^2	1.159	1.164	0.981
R_1; wR_2 ($I \geq 2\sigma$)	0.0293; 0.0796	0.0387; 0.0951	0.0579; 0.0934
R_1; wR_2 (all data)	0.0335; 0.0903	0.0507; 0.1191	0.0999; 0.1091
Residual density (e−/Å^3)	0.701; −0.360	0.547; −0.430	0.590; −0.478

Stirring a solution of dinitrogen complex **5** in *n*-pentane under an atmosphere of CO_2 at −80 °C resulted in the formation of $(^iPr_3P)_2Ni(\eta^2\text{-}CO_2)$ (**7**), as shown in Scheme 2. Complex **7** was characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$NMR spectroscopy. Its infrared spectrum features a strong $\nu_{(CO)}$ band at 1721 cm^{-1}, similar to previously reported $(Cy_3P)_2Ni(CO_2)$ (1740 cm^{-1})[32] and (dtbpe)$Ni(CO_2)$ (1724 cm^{-1}).[31am] Variable-temperature $^{31}P\{^1H\}$ NMR spectra were obtained in toluene-d_8 from 193–293 K and are consistent with a fluxional complex. The singlet observed at δ 36.4 decoalesces below 243 K, and resolves into two doublets, with a $^2J_{PP}$ value of 38.3 Hz. The estimated free activation energy of the dynamic process is 9.5 kcal mol^{-1}.[33] At room temperature, the resonance of the bound CO_2 appears as a triplet at δ 157.4 with $^2J_{PC}$ = 13.2 Hz, which supports an intramolecular exchange mechanism. An intramolecular mechanism has also been postulated by Aresta *et al.* for the dynamic complex $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$.[34]

Crystals of $(^iPr_3P)_2Ni(\eta^2\text{-}CO_2)$ (**7**) suitable for X-ray diffraction were grown from a concentrated *n*-pentane solution at −34 °C, and an ORTEP representation is shown in Scheme 2. The molecular structure is similar to $(PCy_3)_2Ni(\eta^2\text{-}CO_2)$,[26b,35] the first structurally characterized CO_2 adduct of a transition metal. The uncoordinated C(1)–O(2), bond at 1.211(4) Å is typical for a C=O double bond, and the coordinated C(1)–O(1), bond length of 1.265(4) Å indicates a large degree of backbonding from the nickel center into the π* orbital of the ligated C=O unit. The latter distance is significantly longer than the corresponding value of 1.236(1) Å found in a carbonate complex $[MeC(CH_2PPh_2)_3]Ni(\eta^2\text{-}CO_3)$.[36] Other four-coordinate nickel CO_2 complexes have been reported, but have not been crystallographically characterized.[31al,36,37]

A thermal deoxygenation of $(^iPr_3P)_2Ni(\eta^2\text{-}CO_2)$ (**7**) under refluxing conditions (C_6D_6, 16 h) afforded small amounts $(^iPr_3P)_2Ni(CO)_2$ (**8**) and $^iPr_3P{=}O$, together with unknown



Scheme 2 Reactions of **5** with CO_2, CO, and CS_2. Selected bond distances for **7** (Å): Ni(1)–C(1), 1.842(3); Ni(1)–O(1), 1.932(2); Ni(1)–P(1), 2.2806(9); Ni(1)–P(2), 2.1412(9); C(1)–O(1), 1.265(4); C(1)–O(2), 1.211(4). Selected bond angles for **7** (°): P(1)–Ni(1)–P(2), 117.98(3); O(1)–Ni(1)–P(1), 102.39(8), C(1)–Ni(1)–P(2), 100.56(11); O(2)–C(1)–O(1), 136.7(4). Selected bond distances for **8** (Å): Ni(1)–C(1), 1.768(2); Ni(1)–P(1), 2.2370(6); C(1)–O(1), 1.149(2). Selected bond angles for **8** (°): C(1)–Ni(1)–C(1)*, 119.31(13); P(1)–Ni(1)–P(1)*, 119.60(3); C(1)–Ni(1)–P(1), 104.56(6). Selected bond distances for **9** (Å): Ni(1)–Ni(1)*, 4.049(12); Ni(1)–S(1), 2.1648(19); Ni(1)–S(2), 2.1427(18); Ni(1)–C(1), 1.814(6); Ni(1)–P(1), 2.2450(18); C(1)–S(1), 1.662(6); C(1)–S(2)*, 1.660(6). Selected bond angles for **9** (°): C(1)–Ni(1)–S(1), 48.38(18); C(1)–Ni(1)–S(2), 101.89(18); C(1)–Ni(1)–P(1), 158.16(18); S(1)–Ni(1)–P(1), 109.98(7); S(2)–Ni(1)–S(1), 150.15(7); S(2)–Ni(1)–P(1), 99.85(7).

byproducts, as observed by $^{31}P\{^1H\}$ NMR. A similar deoxygenation reaction has been reported for the related species (dtbpe)$Ni(CO_2)$.[31am] The identity of the Ni(0) dicarbonyl **8** was verified by its independent synthesis from the reaction of **5** and CO gas, as shown in Scheme 2. Crystals of complex **8** suitable for solid-state characterization by X-ray crystallography formed slowly after slow evaporation of concentrated *n*-pentane solutions over several weeks at 20 °C. X-ray analysis of the crystalline material confirmed the dicarbonyl Ni(0) complex **8**, and the solid-state molecular structure is depicted in Scheme 2. Compound **8** was also characterized by multinuclear NMR spectroscopy. The room-temperature ^1H NMR spectrum displays the typical multiplicity for the $^iPr_3P$ ligand. The complex displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 53.4 together and a signal in the $^{13}C\{^1H\}$ NMR at δ 202.8 for the coordinated carbonyls. The IR spectrum of **8** shows two very strong bands of nearly equal intensity at 1987 cm^{-1} and 1926 cm^{-1} for the symmetric and asymmetric CO stretches.

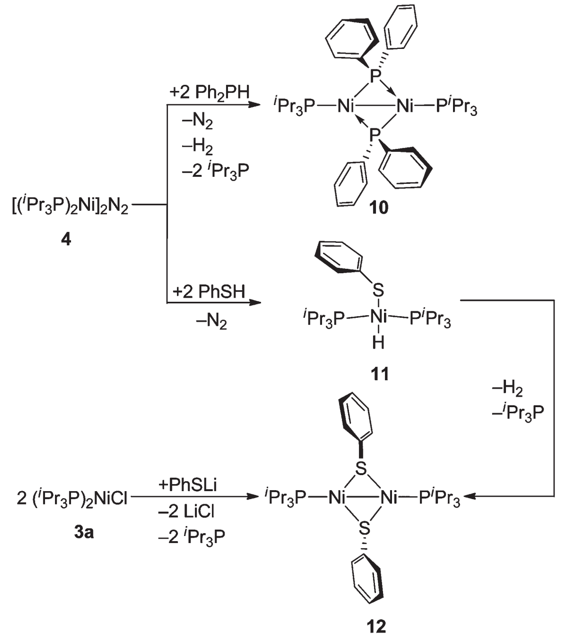
The molecular structure of $(^iPr_3P)_2Ni(CO)_2$ (**8**) and selected intramolecular bond lengths and angles are given in Scheme 2. The coordination is very distorted from ideal tetrahedral angles, with C(1)–Ni–C(1)* and P(1)–Ni–P(1)* angles of 119.31(13)° and 119.60(3)°, respectively. A similar distortion, though to a lesser extent, was also noted for $(PPh_3)_2Ni(CO)_2$.[38] In the related palladium complexes, the OC–Pd–CO angle of 110.7° is much closer to an ideal tetrahedral angle.[39]

While from literature precedent with bulky chelating phosphines[31am] it might be expected that $[(^iPr_3P)_2Ni]_2N_2$ (**5**) would react with CS_2 similarly to CO_2 to provide mononuclear $(^iPr_3P)_2Ni(\eta^2\text{-}CS_2)$, the NMR data give no hint of such a product. Both the solution state and solid-state data are consistent with the dinuclear complex $[(^iPr_3P)Ni(\mu\text{-}\eta^1{:}\eta^2\text{-}CS_2)]_2$ (**9**), as shown in Scheme 2, where **5** acts as a source of the $(^iPr_3P)Ni$ moiety. The isolated reaction product has a $^{31}P\{^1H\}$ NMR spectra with a singlet at δ 45.2. ^1H NMR spectrum shows the typical resonance pattern for a coordinated $^iPr_3P$ ligand. Coordination of CS_2 is indicated in the $^{31}C\{^1H\}$ NMR spectrum, with a signal at δ 125.4.

Crystals of $[(^iPr_3P)Ni(\mu\text{-}\eta^1{:}\eta^2\text{-}CS_2)]_2$ (**9**) suitable for X-ray diffraction were grown from a concentrated 5 : 1 toluene–*n*-pentane mixture at −34 °C. The molecular structure of one of two independent molecules in the unit cell of **9** is shown in Scheme 2. The two $(^iPr_3P)Ni$ fragments, which are related by a crystallographic inversion center, are held together by two CS_2 molecules, so that a six-membered ring is formed. Each CS_2 molecule is η^2 bonded through a C=S linkage to one metal atom and σ-bonded to the other nickel through the second sulfur atom. The coordination environment around each nickel atom is nearly planar. The metal atom is 0.03 Å out of the least-squares plane defined by the four ligated atoms. The chemically different C–S bond distances feature similar lengths, suggestive of extensive π-delocalization. Similar π-delocalization is also known in other dinuclear CS_2 complexes, where only one C=S, group bridges two metal centers.[40] The C(1)–S(1) bond distance is 1.662(6) Å (average of the two independent molecules), which is relatively long compared to the C–S distance of 1.61(1) Å in the monomeric complex (tppme)$Ni(CS_2)$, where tppme = $MeC(CH_2PPh_2)_3$.[41] The infrared spectrum of **9** shows stretches at 1124 and 662 cm^{-1}, which are similar to the values reported from Hillhouse *et al.*[31am] An analogue to **9** with Ph_3P as the supporting phosphine is known,[42] whose structure was only correctly assigned after X-ray crystallographic analysis.[43]

Complex 5 as a precursor to dinuclear Ni(I) complexes

As shown, complex **5** readily reacts with π-acceptors to act as a source of either the $(^iPr_3P)Ni$ or $(^iPr_3P)_2Ni$ fragment, but also readily reacts with substrates with heteroatom–hydrogen bonds such as P–H and S–H bonds to access Ni(I) complexes. For example, when a stoichiometric amount of diphenylphosphine was added to $[(^iPr_3P)_2Ni]_2N_2$ (**5**) in C_6D_6, an immediate complete conversion to dark brown $[(^iPr_3P)Ni(\mu_2\text{-}PPh_2)]_2$ (**10**) was observed by $^{31}P\{^1H\}$ NMR, as shown in Scheme 3. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, but showed no evidence of mononuclear complexes[44] or intermediates arising from oxidative addition. The $^{31}P\{^1H\}$ NMR spectrum features triplet resonances for both the $^iPr_3P$ ligands and the bridging PPh_2 ligand at δ 59.7 and 69.5 with coupling of $^2J_{PP}$ = 30.7 Hz, consistent with a highly symmetric C_{2v} Ni_2P_4-core. There was no appearance of a Ni–H stretch in the IR



Scheme 3 Reactions of **4** and **3a** leading to dinuclear Ni(I) complexes.

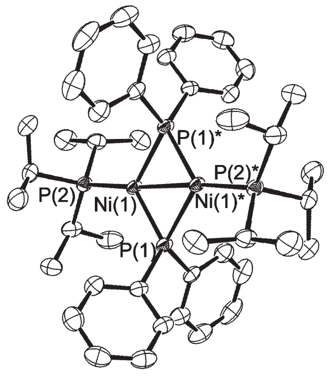


Fig. 2 ORTEP representation of **10** (30% probability ellipsoids) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The labels (*) indicate atom locations generated by a crystallographic inversion centre. Selected bond distances (Å): Ni(1)–Ni(1)*; 2.3702(4); Ni(1)–P(1), 2.0638(5); Ni(1)–P(1)*, 2.2349(5); Ni(1)–P(2), 2.1440(5). Selected bond angles (°): P(1)*–Ni(1)–Ni(1)*, 53.152(15); P(1)–Ni(1)–Ni(1)*, 60.064(16); P(1)–Ni(1)–P(2), 124.23(2); P(2)–Ni(1)–Ni(1)*, 173.92(2); P(2)–Ni(1)–P(1)*, 122.353(19); Ni(1)–P(1)–Ni(1)*, 66.783(16).

spectrum for **10**, which is consistent with its formulation as diphenylphosphido compound.

Complex **10** was isolated by crystallization at −34 °C, and the dark brown hexagonal plates obtained were suitable for X-ray crystallographic characterization. A representation of the solid-state molecular structure is provided in Fig. 2. The molecule possesses a crystallographic center of symmetry at the midpoint of the Ni–Ni bond. The connectivity of **10** is comparable with those of several close analogues;[45] however, a comparison of bond lengths reveals a significant difference. Whereas all previous related structures have nearly symmetrically bridging PR$_2$ moieties with typical Ni–P single bond distances from 2.17–2.19 Å and approximately D_{2h} symmetric Ni$_2$P$_2$ cores, complex **10** feature an approximate C_{2h} core, with asymmetric bridging Ni–P distances of 2.0638(5) and 2.2349(5) Å. The bond lengths suggest the phosphide bridge is behaving as an X$^-$ donor to one nickel centre and an L donor to the other. It is not clear why complex **10** is unique in this regard. The Ni–Ni bonding distance in **10** is 2.3702(4) Å, which is appropriate for a Ni–Ni bond.

The addition of a stoichiometric amount of benzenethiol to a *n*-pentane solution of [(^{i}Pr$_3$P)$_2$Ni]$_2$N$_2$ (**5**) at −34 °C resulted in the formation of *trans*-(^{i}Pr$_3$P)$_2$Ni(SPh)(H) (**11**) which slowly converts to [(^{i}Pr$_3$P)Ni(μ$_2$-SPh)]$_2$ (**12**), as shown in Scheme 3. Complex **11** can be isolated in reasonable yield but is very air-sensitive. In the ^{1}H NMR spectrum **11** features a triplet for the hydride resonance at δ −19.9 with $^2J_{PH}$ = 45.0 Hz. Confirmation of the nickel-bound thiophenolato ligand was established by the change in chemical shift of the phenyl protons, in comparison to those of free benzenethiol. The ^{1}H NMR spectrum and the singlet resonance in the ^{31}P{^{1}H} NMR spectrum at δ 50.9 suggests a square-planar *trans*-phosphine geometry for this complex. The ^{1}H coupled ^{31}P NMR spectrum of **11** is a resolved doublet splitting with $^2J_{PH}$ = 45.0 Hz. The infrared spectrum of **11** has an intense stretch at 1972 cm^{-1} for ν_{Ni-H}, which is similar to the values reported from related bisphosphine Ni–H complexes.[6c,22a,46] Oxidative addition of S–H bonds to nickel have precedent with chelating substrates.[47] The potential use of this reaction for catalytic S–C bond formation[48] is under investigation.

Slow cooling of *n*-pentane solutions yielded crystals of **11** suitable for analysis by X-ray diffraction. Complex **11** exhibits a *trans* square-planar geometry as shown in Fig. 3. The angles about the nickel atom are distorted from an ideal square-planar geometry, similar to **4**. Steric crowding between the triisopropylphosphine and thiophenolato ligands causes the phosphines tilted towards the small hydride group with a P(1)–Ni–P(2) angle of 160.27(3)°. This deviation can be also observed in the related platinum complex *trans*-(Cy$_3$P)$_2$Pt-(SCH═S)(H), obtained from insertion of CS$_2$ into a

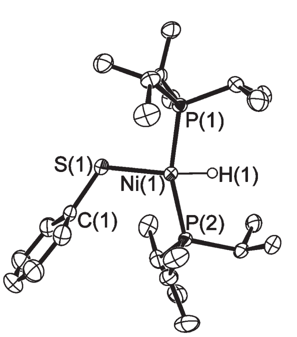


Fig. 3 ORTEP representation of **11** (30% probability ellipsoids) as determined by X-ray crystallography. Hydrogen atoms, except for the hydridic atom H(1), are omitted for clarity. Selected bond distances (Å): Ni(1)–H(1), 1.33(4); Ni(1)–S(1), 2.2046(10); Ni(1)–P(1), 2.1721(9); Ni(1)–P(2), 2.2127(9), S(1)–C(1), 1.776(3). Selected bond angles (°): S(1)–Ni(1)–H(1), 172.7(15); P(1)–Ni(1)–H(1), 80.2(15); P(1)–Ni(1)–P(2), 160.27(3); C(1)–S(1)–Ni(1), 117.13(10).

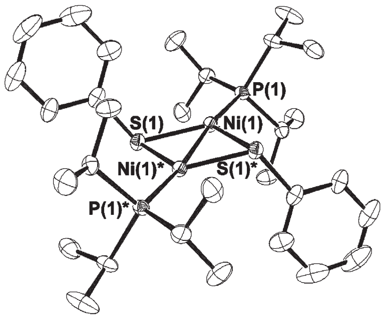


Fig. 4 ORTEP representation of **12** (30% probability ellipsoids) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The * labels indicate atom locations generated by a crystallographic symmetry. Selected bond distances (Å): Ni(1)–Ni(1)*, 2.3660(10); Ni(1)–S(1), 2.1703(11); Ni(1)–S(1)*, 2.1818(13); Ni(1)–P(1), 2.1734(11). Selected bond angles (°): S(1)–Ni(1)–Ni(1)*, 57.30(4); S(1)–Ni(1)–S(1)*, 114.14(4); P(1)–Ni(1)–Ni(1)*, 173.30(4); Ni(1)–S(1)–Ni(1)*, 65.86(4).

$(Cy_3P)_2PtH_2$,[49] as well as other structurally similar hydride complexes such as **4**. The Ni(1)–S(1) distance is 2.2046(10) Å in **11**. The Ni(1)–H(1) distance is 1.33(4) Å, though a more accurate bond length determination requires neutron diffraction data.

Solutions of **11** slowly convert within a period of 3 weeks in *n*-pentane solutions at room temperature by a dimerization that involves the loss of dihydrogen and two phosphine ligands to form $[(^iPr_3P)Ni(\mu_2\text{-}SPh)]_2$ (**12**), as shown in Scheme 3. The ^1H NMR spectra of **11** and **12** are very similar, and the species can be distinguished by the absence of a hydride resonance in **12** and the upfield shift of the singlet resonance to δ 47.5 for the $^iPr_3P$ ligand in the $^{31}P\{^1H\}$ NMR spectra. Complex **12** formed green/brown crystals from *n*-pentane at −34 °C, and the solid-state structure of **12** was determined by X-ray crystallography, and is shown in Fig. 4. The complex features a near coplanar arrangement of the metal centres and their coordinated ligands. The phenyl substituents bend away from the plane, suggestive of a stereochemically active non-bonding pair of electrons on the bridging thiolates. Unlike the Ni–P bond lengths for phosphide complex **10**, the two Ni–S bonds in **12** are similar, with bond lengths of 2.1703(11) and 2.1818(13) Å. Species closely related to **12** have been previously prepared by protonolysis reactions with Ni(I) amido precursors.[50] Ni(I) thiolates have received interest due to their involvement in hydrodesulfurization reactions and as models for enzymes.[50] Mononuclear Ni(I) species have also been obtained from S–H bond oxidative addition, with proposed dinuclear intermediates that support a bimolecular mechanism.[47]

Complex 3a as a precursor to dinuclear Ni(I) complexes

Although the reaction of dinitrogen complex **5** with compounds containing heteroatom-hydrogen bonds is a reasonable synthetic route to Ni(I) complexes such as **10** and **11**, an alternate pathway that obviates the need for highly reactive **5** and instead uses its precursor, **3a**, would be preferable. Indeed, it was found that compound **12** can be prepared more easily from the reaction of PhSLi with $(^iPr_3P)_2NiCl$ in diethyl ether, as shown on the bottom of Scheme 3.

Conclusions

Unlike the heavier late transition metals, the chemistry of Ni complexes supported by $^iPr_3P$ donors is relatively poorly studied. It might be expected that this bulky phosphine might promote analogous nickel chemistry to the similarly sized Cy_3P, but with complexes of greater solubility. In fact, there appears to be significant differences in chemistry, such as the fact that the dinitrogen complex $[(^iPr_3P)_2Ni]_2N_2$ (**5**) maintains a dinuclear structure in pentane, fails to form $(^iPr_3P)_3Ni$, and has an increased propensity to lose a phosphine donor upon reaction with a number of reactants. An example is provided by the equilibrium of **5** in aromatic solvents such as benzene to provide $(^iPr_3P)Ni(\eta^6\text{-}C_6H_6)$ (**6a**). Complex **5** provides an entry into diphosphine Ni(0) adducts such as **7**, **8**, and **9**, as well as Ni(II) complexes such as **11** *via* oxidative addition; however, **5** also provides an entry into Ni(I) chemistry as well as alternate oxidation states, as shown in the reactions that provide **10** and **12**, as well as previously reported reactivity with silanes.[6e] Steric bulk may play a significant role in the loss of $^iPr_3P$ from complexes containing the $(^iPr_3P)_2Ni$ moiety, which may provide either a kinetic or thermodynamic impetus for the formation of Ni(I) complexes such as **10** and **12**. Complex **3a** also appears to be a useful precursor to Ni(I) complexes by salt metathesis. Organometallic dinuclear complexes of the heavier congeners of Ni have become of interest lately in inert bond functionalization,[56] and dinuclear Ni(I) complexes also appear to be of importance in Ni chemistry,[57] including in C–H activation[58] and C–C coupling reactions.[8] Though many Ni-based homogeneous catalyst are assumed to proceed through the 0 and +2 oxidation state, there is considerable precedent for the Ni(I) oxidation state, and 1-electron processes, and have been documented in C–F activation,[6f] cross-coupling,[51] Ziegler Natta polymerization catalysts,[52] and the formation of biaryls from arylnickel(II) precursors[53] amongst other catalytic[10q,54] and enzymatic[59] processes. In some cases the use of non-innocent ligands facilitates 1-electron chemistry,[51j,55] though the formation of **3a–c** from **1a–c** and **2** suggests that Ni(0)/Ni(II) comproportionation to Ni(I) may be common in phosphine supported systems. Further studies are under way to further study the reactivity of **5** as with small molecules and to demonstrate the effective of **3a** as a precursor to Ni(I) complexes *via* salt metathesis.

General procedures

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glove-box. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas; toluene and hexanes were further deoxygenated using a Grubbs' type column system.[1] Benzene-d_6 was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure then trap-to-trap distilled and freeze–pump–thaw degassed three times. Toluene-d_8 was purified in an analogous manner by heating at reflux over Na. THF-d_8 was purified in an analogous manner by heating at reflux over K. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in hertz. ^{1}H NMR spectra were referenced to residual protons (C_6D_5H, δ 7.15; C_7D_7H, δ 2.09; C_4D_7HO, δ 1.73) with respect to tetramethylsilane at δ 0.00. ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4 at δ 0.00. ^{13}C{^{1}H} NMR spectra were referenced relative to solvent resonances (C_6D_6, δ 128.0; C_7D_8, δ 20.4; C_4D_8O, δ 25.37). Infrared spectra (IR) were recorded on a Bruker Tensor 27 operating from 4000–400 cm^{-1}. High Resolution Mass Spectroscopy (HRMS) was performed at McMaster University, Hamilton, Ontario, Canada. Elemental analyses were performed at the Center for Catalysis and Materials Research, Windsor, Ontario. Raman spectra were recorded from on both a Bruker multi-RAM Fourier transform Raman and a Renishaw inVia Raman microscope using 785 nm laser line excitation. The compounds benzene-d_6, toluene-d_8, and THF-d_8 were purchased from Cambridge Isotope Laboratory. Magnesium turnings were vigorously dry stirred over 8 hours to create a reactive surface prior to use. Triisopropylphosphine was purchased from STREM and butyl-lithium and lithium triethylborohydride from Aldrich, and were used without further purification.

Synthesis and characterization of 1a–c. General procedure: A heterogeneous mixture of anhydrous NiX_2 (X = Cl, Br, I) (0.023–0.038 mol, 3–5 g) in 100 mL toluene was stirred in the presence of two equivalents of $^iPr_3P$ (0.048–0.080 mol, 7.68–12.81 g) in 5% excess. The color of the mixture turned dark red within a period of 3 days. The mixture was filtered through a glass frit and the residue washed with 30 mL *n*-pentane. The toluene was removed under vacuum affording dark red crystals suitable for X-ray diffraction. Combined isolated products afforded $(^iPr_3P)_2NiX_2$ (X = Cl, Br, I) (**1a–c**) in almost quantitative yields. (9.3 g–16.2 g, 90–95% yield). $(^iPr_3P)_2NiCl_2$ (**1**); Anal Calcd for $C_{18}H_{42}Cl_2NiP_2$ (450.07): C, 48.04; H, 9.41; Found C, 47.84; H, 9.81. $(^iPr_3P)_2NiBr_2$ (**2**); IR (Nujol, KBr): 1294 vw, 1240 s, 1156 m, 1093 m, 1055 s, 1029 s, 963 vw, 924 m, 881 s, 723 w, 653 vs, 568 m, 517 s, 433 w cm^{-1}. Anal Calcd for $C_{18}H_{42}Br_2NiP_2$ (538.98): C, 40.11; H, 7.85; Found: C, 39.46 H, 8.14. $(^iPr_3P)_2NiI_2$ (**3**): IR (Nujol, KBr): 1385 s, 1296 m, 1244 s, 1158 m, 1092 m, 1061 s, 1032 s, 963 w, 927 m, 884 s, 640 vs, 600 m, 522 s, 480 w, 433 w cm^{-1}. Anal Calcd for $C_{18}H_{42}I_2NiP_2$ (632.98): C, 34.15; H, 6.69; Found: C, 34.30; H, 6.99. ^{1}H NMR (**1a–c**) (298 K, C_6D_6, 500 MHz): δ 1.2–1.4 (d, $^3J_{HH}$ = 7.0 Hz, 36H, $CH(CH_3)_2$), 2.2–2.4 (septet, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CHMe_2)$. ^{13}C{^{1}H} NMR (298 K, C_6D_6, 75.5 MHz): δ 20.2 (s, $P(CH(CH_3)_2)_3$), 23.1 (br s, $P(CH(CH_3)_2)_3$).

Synthesis and characterization of 2. A mixture of $(^iPr_3P)_2NiCl_2$ (**1a**) (2.50 g, 5.55 mmol) and an six fold excess of magnesium (740 mg, 30.4 mmol) was combined in 200 mL THF at 20 °C in the presence of 1 atm ethylene atmosphere. After 3 h the dark red mixture turned yellow and all volatiles were removed under vacuum. The product was extracted with *n*-pentane (2 × 50 mL) and $MgCl_2$ was filtered off. The product isolated by removing the *n*-pentane under vacuum, which provided **2** (1.87 g, 83%) as a yellow powder in sufficient purity for further use. Complex **2** crystallized as orange plates and cubes from *n*-pentane solutions at −34 °C. Almost quantitative yields were observed using $(^iPr_3P)_2NiBr_2$ (**1b**) and $(^iPr_3P)_2NiI_2$ (**1c**) in lieu of **1a**. **Method B**: A 100 mL Schlenk flask was charged with a 30 mL *n*-pentane solution of **5** (170 mg, 0.216 mmol). The solution was cooled to −80 °C, and stirred for 5 min under the atmosphere of ethylene. The dark red color lightened to yellow-orange immediately. After the solution warmed to ambient temperature, all volatiles were removed under vacuum. The residue was dissolved in 2 mL *n*-pentane and crystallized at −34 °C to afford 161 mg (91%) of **2**. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.19 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.1 Hz, 36H, $P(CH(CH_3)_2)_3$), 2.02 (sept, $^3J_{HH}$ = 7.1 Hz, 6H, $P(CH(CH_3)_2)_3$); 2.06 (s, 4H, $CH_2{=}CH_2$). ^{13}C{^{1}H} NMR (298 K, C_6D_6, 75.5 MHz): δ 20.7 (s, $P(CH(CH_3)_2)_3$), 27.1 (vt, $^1J_{PC} + {}^3J_{PC}$ = 15.5 Hz, $P(CH(CH_3)_2)_3$), 37.1 (vt, $^2J_{PC}$ = 12.1 Hz, $NiCH_2{=}CH_2$). ^{31}P{^{1}H} NMR (298 K, C_6D_6, 121.5 MHz): δ 51.8 (s, 2P). IR (Nujol, KBr): 1360 m, 1296 vw, 1241 m, 1183 m, 1157 w, 1090 w, 1051 m, 1028 m, 961 vw, 922 w, 880 s, 723 vw, 644, vs, 605 m, 564 m, 523 s, 476 vw, 449 m, 417 m cm^{-1}. Anal Calcd for $C_{20}H_{46}NiP_2$ (407.22): C, 58.99; H, 11.39; Found C, 58.25; H, 11.14.

Synthesis and characterization of 3a–c. General procedure: To a heterogeneous mixture of $(^iPr_3P)_2NiCl_2$ (1.50 g, 3.33 mmol) in 50 mL *n*-pentane, was added 1.1 equivalents of **2** (1.49 g, 3.66 mmol) at 20 °C. After stirring the mixture for 3 h (30 min for **3b**, 5 min for **3c**) at 20 °C the solvent was removed under vacuum and the grayish residue washed with 10 mL cold *n*-pentane (−34 °C) to remove excess **2**. The residue of $(^iPr_3P)_2NiX$ (X = Cl, Br, I) (**3a–c**) was taken up in *n*-pentane at 20 °C and cooling to −34 °C afforded colorless crystals in a yield of 2.21–2.37 g (80–86%). Recrystallization of concentrated solutions of **3a–c** at −34 °C in *n*-pentane afforded cubic crystals suitable for X-ray diffraction. For $(^iPr_3P)_2NiCl$ (**3a**): ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 3.1 (br, 36 H, $P(CH(CH_3)_2)_3$), 55. (br, 6H, $P(CH(CH_3)_2)_3$). Magnetic susceptibility (Evans method, 298 K, toluene): $\mu_{eff} \sim 2.05\ \mu_B$. IR (Nujol, KBr): 1293 w, 1240 s, 1156 m, 1094 m, 1054 s, 1029 s, 963 vw, 924 m, 882 vs, 722 w, 655 vs, 600 vw, 569 m, 517 s, 433 w, 411 vw cm^{-1}. Anal Calcd for $C_{18}H_{42}ClNiP_2$ (414.62): C, 52.14; H, 10.21; Found C, 52.73; H, 10.66. For $(^iPr_3P)_2NiBr$ (**3b**): ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 3.0 (br(s), $W_{1/2}$ = 170 Hz, $P(CH(CH_3)_2)_3$); ^{31}P{^{1}H} NMR (298 K, C_6D_6, 121.5 MHz): no signal. Magnetic susceptibility (Evans method, 298 K, toluene): $\mu_{eff} \sim 2.14\ \mu_B$. IR (Nujol, KBr): 1294 vw, 1240 s, 1156 m, 1093 m, 1055 s, 1029 s, 963 vw, 924 m, 881 s, 723 w, 653 vs, 568 m, 517 s, 433 w cm^{-1}. Anal Calcd for $C_{18}H_{42}BrNiP_2$ (459.07): C, 47.09; H, 9.22; Found C, 47.21; H, 9.97. For $(^iPr_3P)_2NiBr$ (**3c**): ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 2.98 (br(s), $W_{1/2}$ = 150 Hz, $P(CH(CH_3)_2)_3$); $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): no signal. Magnetic susceptibility (Evans method, 298 K, toluene): $\mu_{eff} \sim 2.19\ \mu_B$. IR (Nujol, KBr): 1295 w, 1240 m, 1156 w, 1092 w, 1056 m, 1029 m, 925 w, 881 s, 800 w, 722 w, 652 vs, 608 w, 568 w, 518 s, 432 w cm^{-1}. Anal Calcd for $C_{18}H_{42}INiP_2$ (506.07): C, 42.72; H, 8.37; Found C, 42.97; H, 8.49.

SYNTHESIS AND CHARACTERIZATION OF 4. A solution of 1.0 M $LiEt_3BH$ (0.37 mL, 0.377 mmol) was added dropwise to a −34 °C solution of $(^iPr_3P)_2NiCl_2$ (170 mg, 0.377 mmol) in THF. The dark red solution was warmed to ambient temperature within a period of 30 min and removal of THF under vacuum afforded a brown orange powder. The residue was taken up in ice-cold *n*-pentane and filtered through a plug of Celite to remove $(^iPr_3P)_2NiCl$ (**3a**) as a byproduct. The residue was recrystallized from *n*-pentane at −34 °C and afforded orange yellow plates of **4** (40 mg, 25%) suitable for X-ray diffraction. **Method B**: A mixture of stoichiometric amounts of $(^iPr_3P)_2NiCl_2$ (200 mg, 0.44 mmol) and NaH (10.6 mg, 0.44 mmol) in THF was stirred at ambient temperature for 3 h. The solvent was removed under vacuum and the residue was extracted with *n*-pentane (2 × 10 mL) and filtered through a plug of Celite. The concentrated solution was kept at −34 °C for 30 min and the precipitate $(^iPr_3P)_2NiCl$ (**3a**) removed from the mother liquor. The *n*-pentane solution was concentrated and crystallized at −34 °C to afford 31 mg (17%) of **5**. ^1H NMR (298 K, C_6D_6, 500 MHz): δ −24.3 (t, $^2J_{PH}$ = 72.0 Hz, 1H, Ni–H), 1.22 (dd, $^3J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 6.0 Hz, 36H, $P(CH(CH_3)_2)_3$) 2.03 (sept, $^3J_{HH}$ = 6.0 Hz, 6H, $P(CH(CH_3)_2)_3$). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 49.5 (s, 2P). IR (Nujol, KBr): 1928 s, 1364 vs, 1292 m, 1241 s, 1180 s, 1154 s, 1093 m, 1059 s, 1029 s, 964 vw, 927 m, 884 vs, 799 w, 759 m, 699 m, 658 vs, 618 m, 575 vw, 525 s, 477 w, 431 w. Anal Calcd for $C_{18}H_{43}ClNiP_2$ (415.63): C, 52.02; H, 10.43; Found C, 52.15; H 10.67.

SYNTHESIS AND CHARACTERIZATION OF 5. A mixture of $(^iPr_3P)_2NiCl$ (**3a**) (1.5–2.5 g, 3.6–6.03 mmol) and an excess of magnesium (400–850 mg, 16.4–34.9 mmol) were stirred at 20 °C in 20 mL THF for 2 h. After the mixture turned blood red the volatiles were removed under vacuum and extracted with 50 mL *n*-pentane and filtered through a sinter disc with a plug of Celite to remove $MgCl_2$. The solvent was removed under vacuum to provide a dark red, waxy solid (1.10–2.01 g, 78–85% yield) of **5**. Crystals in the form of dark red plates, suitable for X-ray diffraction, were isolated from a sample of 50 mg dissolved in 0.5 mL HMDSO (hexamethyldisiloxane) by cooling to −34 °C. ^1H NMR (298 K, C_6D_6, 500 MHz): δ 1.19 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.1 Hz, 72H, $P(CH(CH_3)_2)_3$) 2.02 (sept, $^3J_{HH}$ = 7.1 Hz, 12H, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 20.7 (s, $P(CH(CH_3)_2)_3$), 27.1 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 16.6 Hz, $P(CH(CH_3)_2)_3$). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 43.7 (s, 4P). $^{15}N\{^1H\}$ NMR (298 K, C_5H_{12}, 30.5 MHz): δ −71.2 (s(br), $W_{1/2}$ = 15 Hz, 2N, NiN_2). IR (Nujol, KBr): 1236 s, 1155 m, 1090 m, 1039 s, 1021 s, 922 m, 880 s, 646 vs, 601 vs, 545 s, 516 m, 475 s cm^{-1}. Raman (solid and pentane solution): 1908 cm^{-1}. Anal Calcd for $C_{36}H_{84}N_2Ni_2P_4$ (786.35): C, 54.99; H, 10.77; N, 3.56; Found C, 54.73; H 10.90; N, 2.91. The low nitrogen value may reflect the high reactivity of **5** towards N_2 dissociation.

EQUILIBRIUM REACTION OF 5 IN BENZENE OR TOLUENE TO PROVIDE 6A, B. Dark red **5** (39 mg, 0.5 mmol) was dissolved in *n*-pentane (0.6 mL) and d_6-benzene or d_8-toluene (0.1 mL) added in a J. Young tube and the sample was analyzed by NMR spectroscopy after a period of 5 min. The ^{31}P NMR spectra revealed a mixture of **6a** (or **6b**), **5** and $^iPr_3P$ in a ratio of (40 : 20 : 40) respectively. When the deuterated solvent was removed *in vacuo* and dissolved again in *n*-pentane, **5** is reformed quantitatively. Detailed NMR data for **6a,b** have been previously reported.[6c]

SYNTHESIS AND CHARACTERIZATION OF 7. A solution of **5** (150 mg, 0.191 mmol) in 20 mL *n*-pentane was exposed to 1 atm 99% carbon dioxide at −50 °C. The solution turned immediately from dark red to orange. After stirring for 15 min at room temperature the solution was cooled to −78 °C, which caused the product to slowly precipitate. The solution was decanted and the residue taken up in 2 mL ice-cold *n*-pentane. At −34 °C red crystals (needles) were deposited in a yield of 44%. ^1H NMR (298 K, C_6D_6, 500 MHz): δ = 1.05 (dd, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.75 (sept, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.5 (AMM′, $^1J_{PC}$ = 19.3 Hz, $^3J_{PC}$ = 10.4 Hz, $P(CH(CH_3)_2)_3$), 24.3 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 17.7 Hz, $P(CH(CH_3)_2)_3$), 157.4 (t, $^2J_{PC}$ = 13.2 Hz Ni–CO_2). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 49.3 (s, 2P). $^{31}P\{^1H\}$ NMR (193 K, C_6D_6, 121.5 MHz): δ 31.6 (d, $^2J_{PP}$ = 38.3 Hz, 1P), 63.5 (d, $^2J_{PP}$ = 38.3 Hz, 1P). IR (Nujol, KBr): 2039 vw, 1909 vs, 1721 s, 1670 s, 1239 m, 1181 m, 1154 m, 1092 w, 1044 m, 1025 s, 961 vw, 925 m, 882 s, 832 w, 698 w, 652 vs, 606 m, 544 w, 521 m 475 m. Anal Calcd for $C_{19}H_{42}NiO_2P_2$ (423.18): C, 53.93; H, 10.00; Found C, 53.85; H 9.87.

SYNTHESIS AND CHARACTERIZATION OF 8. Complex **5** (157 mg, 0.20 mmol) was dissolved in diethyl ether (10 mL) and cooled to −78 °C. The solution was exposed to 1 atm of carbon monoxide and stirred for 5 min. After the deep red color disappeared and the reaction mixture reached ambient temperature, the solvent was removed under vacuum and the grey solid of **8** isolated, washed with ice-cold *n*-pentane (3 mL) and dried under vacuum (154 mg, 89% yield). Single crystals suitable for X-ray diffraction of **8** were obtained when concentrated *n*-pentane solutions were recrystallized at 20 °C. ^1H NMR (298 K, C_6D_6, 500 MHz): δ 1.13 (dd, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 6.9 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.75 (sept, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.8 (s, $P(CH(CH_3)_2)_3$), 25.9 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 13.6 Hz, $P(CH(CH_3)_2)_3$), 202.8 (s(br), Ni–CO). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 53.4 (s, 2P). IR (Nujol, KBr): 1987 vs, 1926 vs, 1302 vw, 1241 m, 1154 w, 1089 m, 1075 w, 1045 w, 1032 s, 961 w, 922 m, 882 s, 722 vw, 654 s, 632 s, 591 vs, 501 m, 482 m, 460 s. Anal Calcd for $C_{20}H_{42}NiO_2P_2$ (435.19): C, 55.20; H, 9.73; Found C, 54.96; H 10.54.

SYNTHESIS AND CHARACTERIZATION OF 9. A stirred pentane solution of **5** (180 mg, 0.229 mmol) was cooled to −80 °C and carbon disulfide (34.7 mg, 0.46 mmol) was added in a dropwise fashion. The solution immediately turned orange brown. After the solution warmed to ambient temperature, all volatiles were removed under vacuum and the brownish residue washed with cold *n*-pentane, dissolved in 5 mL toluene and filtered through a plug of Celite. Red crystals suitable for X-ray diffraction studies were obtained by recrystallization from a solvent mixture (toluene–pentane) 5 : 1 at −34 °C. Yield (97 mg, 72%). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.05 (dd, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.75 (sept, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 19.5 (s, $P(CH(CH_3)_2)_3$), 23.5 (d, $^1J_{PC}$ = 17.3 Hz, $P(CH(CH_3)_2)_3$), 125.4 (s, Ni–CS_2). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 45.2 (s, 2P). IR (Nujol, KBr): 1596 m, 1239 w, 1173 vw, 1124 vs, 1056 m, 1028 m, 923 w, 881 m, 721 s, 662 s, 574 w, 526 s. Anal Calcd for $C_{20}H_{42}Ni_2P_2S_4$ (590.14): C, 40.70; H, 7.17; Found C, 40.72; H 6.77.

Synthesis and characterization of 10. A 110 mg sample of **5** (0.14 mmol) was dissolved in 2 mL *n*-pentane and slowly combined at 25 °C with diphenylphosphine (52 mg, 0.279 mmol) in 2 mL *n*-pentane. After 1 h stirring the solution was dried under reduced pressure and the remaining oil dissolved in 1 mL *n*-pentane. At −34 °C dark brown crystalline hexagonal plates of **10** were formed (88 mg, 78% yield). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 0.98 (dd, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 6.9 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.82 (sept, $^3J_{HH}$ = 6.9 Hz, 6H, $P(CH(CH_3)_2)_3$), 7.02–7.07 (m, 4H, Ar–H), 7.11–7.16 (m, 8H, Ar–H), 7.89–7.95 (m, 8H, Ar–H). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 20.1 (s, $P(CH(CH_3)_2)_3$), 24.8 (vt, $^1J_{PC} + {^3J_{PC}}$ = 16.5 Hz, $P(CH(CH_3)_2)_3$), 126.2 (s, Ar–CH), 127.5 (s, Ar–CH), 133.0 (t, $^2J_{PC}$ = 6.8 Hz, Ar–CH), 144.0 (t, $^1J_{PC}$ = 9.5 Hz, Ar–C). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 59.7 (t, $^2J_{PP}$ = 30.7 Hz, 2P), 69.5 (t, $^2J_{PP}$ = 30.7 Hz, 2P, $NiPPh_2$). Anal Calcd for $C_{42}H_{62}Ni_2P_4$ (808.2): C, 62.41; H, 7.73; Found C, 62.73; H, 8.00.

Synthesis and characterization of 11. A dark red solution of **5** (150 mg, 0.19 mmol) in 5 mL *n*-pentane was cooled to −34 °C and thiophenol (41 mg, 0.38 mmol) was added in dropwise fashion. The solution lightened to yellow immediately and gas evolution (N_2) was observed. After the solution warmed to ambient temperature, the solution was reduced half the volume and cooled to −34 °C to afford orange crystals of **11** (97 mg, 52%) suitable for X-ray diffraction. ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ = −19.9 (t, $^2J_{PH}$ = 45.0 Hz, 1H, Ni–H), 1.21 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.1 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.87 (sept, $^3J_{HH}$ = 7.1 Hz, 6H, $P(CH(CH_3)_2)_3$), 7.03 (t, $^3J_{HH}$ = 7.1 Hz, 1H, Ar–H), 7.14 (t, $^3J_{HH}$ = 7.1 Hz, 2H, Ar–H), 7.89 (dd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, Ar–H), $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 20.7 (s, $P(CH(CH_3)_2)_3$), 24.9 (vt, $^1J_{PC} + {^3J_{PC}}$ = 21.1 Hz, $P(CH(CH_3)_2)_3$), 122.1 (s, Ar–CH), 126.8 (s, Ar–CH), 133.3 (s, Ar–CH), 151.8 (t, $^3J_{PC}$ = 6.6 Hz, Ar–C) $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 50.9 (s, 2P). ^{31}P NMR (298 K, C_6D_6, 121.5 MHz): δ 50.9 (d, $^2J_{PH}$ = 45.0 Hz, 2P). IR (Nujol, KBr): 3054 m, 1972 s, 1573 s, 1295 vw, 1253 m, 1157 w, 1082 s, 1051 m, 1022 s, 925 m, 881 m, 762 s, 740 vs, 699 s, 670 vs, 614 vs, 492 m, 447 vw. Anal Calcd for $C_{24}H_{48}NiP_2S$ (489.34): C, 58.91; H, 9.89; Found C, 58.53; H 10.22.

Synthesis and characterization of 12. A solution of PhSiLi, obtained from a solution of butyl-lithium 1.0 M (0.22 mL, 0.36 mmol) combined with benzenethiol (40 mg, 0.36 mmol) in Et_2O, was added to a stirred diethyl ether solution of 150 mg $(^iPr_3P)_2NiCl$ (0.36 mmol) at −34 °C. After 1 h the volatiles were removed *in vacuo* and the residue extracted with *n*-pentane (2 × 10 mL) and filtered through a plug of Celite (113 mg, 48%). **Method B**: A dark red solution of **5** (90 mg, 0.114 mmol) was combined at room temperature with two equivalents benzenethiol (25 mg, 0.23 mmol) in toluene an heated for 16 h at 70 °C. The solvent was removed under vacuum and upon recrystallization of the remaining oil from *n*-pentane solutions, greenish-brown X-ray quality crystals of **12** were obtained (24 mg, 32%). ^{1}H NMR (298 K, C_6D_6, 500 MHz): δ 1.12 (dd, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 7.2 Hz, 36H, $P(CH(CH_3)_2)_3$), 1.66 (sept, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CH(CH_3)_2)_3$), 6.97 (apparent dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, Ar–H), 8.16 (apparent dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 4H, Ar–H). $^{13}C\{^1H\}$ NMR (298 K, C_6D_6, 75.5 MHz): δ 20.1 (s, $P(CH(CH_3)_2)_3$), 23.8 (vt, $^1J_{PC} + {^3J_{PC}}$ = 16.7 Hz, $P(CH(CH_3)_2)_3$), 124.7 (s, Ar–CH), 131.1 (s, Ar–CH), 135.7 (s, Ar–CH), 143.1 (s, Ar–C). $^{31}P\{^1H\}$ NMR (298 K, C_6D_6, 121.5 MHz): δ 47.5 (s, 2P). Anal Calcd for $C_{30}H_{52}Ni_2P_2S_2$ (656.20): C, 54.91; H, 7.99; Found C, 54.81; H 8.04.

X-ray crystallography

The X-ray structures were obtained at low temperature, with the crystals covered in Paratone and placed rapidly into the cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using the SMART[60] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10–30 s per frame. Data reductions were performed using the SAINT[61] software, and the data were corrected for absorption using SADABS.[62] The structures were solved by direct or Patterson's methods using SHELXS-97[63] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97[63] and the WinGX[64] software package, and thermal ellipsoid plots were produced using ORTEP32.[65] Multiple attempts to collect data on monoclinic **5** were suggestive of a twinned structure, which provides an apparent orthorhombic cell with a = 15.79(2), b = 26.84(4), c = 10.78(2). The data was modeled as a two component twin. Additional problems with the data resulted from the disorder of several donors P^iPr_3, which were modeled as best as possible. As a result the structure is of modest quality. Crystallographic.cif can be obtained from the CCDC (CCDC 896745–896759).

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