# **ORGANOMETALLICS**

# Bridged and Unbridged Nickel–Nickel Bonds Supported by Cyclopentadienyl and Phosphine Ligand Sets

Peter A. Cleaves, Alexander J. Ayres, Lisa Vondung, John C. Stewart, Philip J. Cobb, Ashley J. Wooles, and Stephen T. Liddle\*



and characterized. From these complexes, the synthesis of the Ni complexes [NiCl(PR<sub>3</sub>)( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>R')] R = Me, R' = H (**3-Me**), R= "Bu, R' = H (**3-Me**), R = "Pr, R' = H (**3-"Pr**), R = Et, R' = Me (4), and R = Et, R' = SiMe<sub>3</sub> (5) was achieved. All complexes were fully characterized, including single crystal X-ray crystallography. Complexes **3-R**, **4**, and **5** were then used to obtain homobimetallic Ni complexes with rare examples of unbridged Ni–Ni bonds [{Ni( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)(PR<sub>3</sub>)}<sub>2</sub>], with R = Me (7-Me) and R = "Pr (7-"Pr) being structurally characterized by single crystal X-ray diffraction. In order to probe the effect of bridging ligands on



the Ni–Ni bond, the bridged complex  $[{Ni(\mu:\eta^5-C_5H_4CH_2CH_2P({}^{t}Bu_2))_2}]$  (8) was synthesized from the monomeric precursor  $[Ni(Cl)(\kappa^1-\eta^5-C_5H_4CH_2CH_2P^{t}Bu_2)]$  (6). The Ni–Ni distances in 7-Me, 7-<sup>n</sup>Pr, and 8 were found to be 2.407(1), 2.3931(6), and 2.6027(17) Å, respectively, the latter seemingly lengthened compared to the other two due to the tethered nature of the bridging ligand. DFT calculations confirm the presence of unbridged  $\sigma$ -bonds between the Ni atoms in 7-Me and 7-<sup>n</sup>Pr and show that the bridging ligand in 8 has a minimal effect on the character of the Ni–Ni bond.

# INTRODUCTION

Bimetallic complexes with direct metal–metal (M-M) bonds have drawn intense interest since the 1960s, since they provide interesting examples for extending bonding concepts.<sup>1</sup> Such M-M units can be viewed as intermediate between the smallest unit of mononuclear metal complexes to clusters, and ultimately bulk metals.<sup>2</sup> Accordingly, they often possess unique properties and so are of interest across various fields, such as mimicking and understanding metal surface catalysis reactions, as structural subunits of metal–organic frameworks, photosensitizers, in bio-inorganic chemistry, or materials chemistry.<sup>1,3,4</sup> In the area of homogeneous catalysis, bimetallic complexes with direct M-M interactions are increasingly receiving attention.<sup>5,6</sup> This interest is driven by the unusual synergic reactivity of two metals in close proximity that often cannot be achieved with monometallic congeners.<sup>7–10</sup>

Due to rising costs and sustainability concerns, many efforts have been made in recent years to move away from Pd and Pt to more abundant 3d metals.<sup>11</sup> As the lightest group 10 homologue, Ni is thus increasingly targeted as an alternative to Pd- and Pt-based catalysts, and Ni-Ni complexes have shown promising activities.<sup>10,12,13</sup> Besides the burgeoning application of Ni-Ni complexes as catalysts, they are promising starting materials for the synthesis of heterobimetallic complexes, which are of increasing interest.<sup>14</sup> The combination of early and late transition metals allows for the facile activation of polar bonds. The synthesis of such complexes requires unbridged Ni-Ni complexes as starting materials. Ideally, they should be accessible by facile synthetic routes and allow for easy variation of ligands. However, whilst unbridged homobimetallic complexes are known for many transition metals,<sup>1,3</sup> the number of examples for Ni is limited. A vast majority of Ni-Ni complexes contain bridging ligands or larger  $\pi$ -systems which enable a positive bonding interaction between the monomers.<sup>15,16</sup>

Prior to this work, only three clear-cut examples of Ni–Ni bonds without bridging ligands had been reported (Figure 1). A few more seemingly unbridged Ni-Ni complexes are known, but closer inspection reveals ligand–ligand bonding interactions.<sup>15</sup> The first example of an unbridged Ni-Ni complex was  $K_4[Ni_2(CN)_6]$ , which has a short Ni–Ni bond length of 2.32 Å.<sup>17</sup> Two organometallic complexes were subsequently reported, both supported by cyclopentadienyl and phosphines

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Figure 1. Known complexes with an unbridged Ni-Ni bond.<sup>15-19</sup>

or bulky isocyanide ligands.<sup>18,19</sup> Figueroa's complex was obtained by reaction of nickelocene with an aryl isocyanide ligand. Notably, reduction of the steric bulk of the aryl group yields a dimeric complex with bridging isocyanides. Wilke's complex was obtained by a different route, reducing  $[(\eta^5-Cp)Ni(PEt_3)Cl]$  with activated Mg. However, bulkier PPh<sub>3</sub> and C<sub>5</sub>Me<sub>5</sub> analogues proved elusive. These examples show that ligand bulkiness and the reducing agent must be carefully chosen to obtain unbridged Ni-Ni complexes.

With the increasing interest in Ni-Ni complexes generally and our interest in preparing M–M bonds where one metal is an f-element, we set out to explore dimeric Ni complexes more

Scheme 1. General Synthetic Route to Ni Complexes<sup>a</sup>

systematically in light of their general paucity. Our aim was to establish a modular synthetic route to allow for easy variation of substituents, and the ready steric and electronic tunability of phosphines and cyclopentadienyls led us to use them in this study. Furthermore, we investigated a tethered cyclopentadienyl-phosphine system for comparison. Here, we report the results of this study which has yielded a range of Ni precursors and three new Ni-Ni complexes, where two are unbridged and one is bridged.

# RESULTS AND DISCUSSION

**Synthetic Approach.** Attempting to systematically probe the steric and electronic effects of substituents, we prepared a range of  $[NiCl(PR_3)(\eta^5-C_5H_4R')]$  complexes (Scheme 1). The complexes  $[NiCl_2(PR_3)_2]$  (1-R, R = Et, "Bu) have previously been reported in the literature, but the R = Me, "Pr variants have surprisingly not previously been described.<sup>20</sup> Nickelocene 2-H, complex 3-Et, and the Ni-Ni complex 7-Et have been reported previously, but are included here for completeness.<sup>18,20–22</sup>

Additionally, we utilized 6 with a tethered cyclopentadienyl phosphine ligand as a precursor to a bridged Ni-Ni complex 8 (Scheme 2) in order to provide comparisons between bridged and unbridged Ni-Ni complexes. The methodology is essentially the same for both schemes, with the principal change being whether the cyclopentadienyl-phosphine combination is tethered or not.

**Synthesis of Ni Complexes 1-R.** The complexes  $[Ni(Cl)_2(PR_3)_2]$  (R = Me, 1-Me; R = "Pr, 1-"Pr) were obtained as red crystalline solids in good yields (75% and 58%, respectively) by the reaction of NiCl<sub>2</sub> with the appropriate phosphine (Scheme 1). An initial color change from orange to dark blue was observed upon the addition of PMe<sub>3</sub> to NiCl<sub>2</sub>, which is attributed to the formation of  $[Ni(Cl)_2(PMe_3)_3]$ , as reported by Sun and co-workers.<sup>24</sup>  $[Ni(Cl)_2(PMe_3)_3]$  was



<sup>a</sup>Complexes 1-Et, 1-<sup>n</sup>Bu, 2-H, 3-Et, and 7-Et have been reported previously.<sup>18,20-22</sup>

Scheme 2. Synthesis of 6 As Taken from ref 23 and Reduction to the Bridged Ni-Ni Complex 8



noted to be thermally unstable, resulting in the dissociation of a  $PMe_3$  ligand to afford **1-Me** upon heating. The solid state molecular structures of **1-Me** and **1-**<sup>*n*</sup>**Pr** were determined to confirm their formulations (Figure 2).



Figure 2. Solid state structures of complexes (a) 1-Me and (b) 1-"Pr at 90 K with selective labeling. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: 1-Me: Ni1–P1 2.2262(6), Ni1–Cl1 2.1596(5), P1–Ni1–P1a 180.00; 1-"Pr Ni1–P1 2.232(6), Ni1–P2 2.2260(5), Ni1–Cl1 2.1658(5), Ni1–Cl2 2.1578(5), P1–Ni1–P2 178.63(2).

X-ray Diffraction and NMR Analysis of Ni Complexes 1-R. The 16-electron Ni(II) complexes 1-Me and 1-"Pr adopt the anticipated square planar coordination geometries (sum of bond angles around Ni ~ 360°), with the phosphine ligands *trans* to each other in each complex. The average Ni–P and Ni–Cl distances in 1-Me (2.2263(6) and 2.1596(5) Å) and 1-"Pr (2.2293(6) and 2.1618(5) Å) compare well to the previously reported compound  $[Ni(Cl)_2(PEt_3)_2]$ , 1-Et (2.2329(5) and 2.1628(5) Å).<sup>25</sup> For 1-"Bu, only spectroscopic data and no solid state structure has been reported.<sup>20</sup>

Single resonances were observed in the  ${}^{31}P{}^{1}H$  NMR spectra of both 1-Me (-23.1 ppm) and 1-"Pr (-3.2 ppm),

which is in line with two equivalent phosphorus atoms in each complex. The observed downfield shifts compared to the free  $PR_3$  ligands ( $\delta(PMe_3) = -62 \text{ ppm}$ ,  $\delta(P^nPr_3) = -33 \text{ ppm}$ ) are in line with the expected decrease of electron density at the phosphorus atom upon coordination of  $PR_3$  to the nickel atom.

Article

Synthesis and X-ray Diffraction Analysis of Nickelocene Derivatives 2-R. The nickelocene derivatives  $[Ni(\eta^5-C_5H_4R')_2]$  (R' = Me, 2-Me; R' = SiMe<sub>3</sub>, 2-SiMe<sub>3</sub>) were prepared via the reaction of  $[Ni(NH_3)_6]Cl_2$  with 2 equivalent of either  $[Na(C_5H_4Me)]$  or  $[K(C_5H_4SiMe_3)]$ . Following workup, 2-Me was purified via sublimation to afford dark green crystals (23% yield), and 2-SiMe<sub>3</sub> was crystallized from *iso*-hexane to afford a dark green microcrystalline solid (31% yield). Unfortunately, despite repeated attempts, crystals of 2-SiMe<sub>3</sub> suitable for single crystal X-ray diffraction studies could not be prepared; however, the solid state structure of 2-Me could be determined and is shown in Figure 3. The methyl



Figure 3. Solid state structure of complex 2-Me at 90 K with selective labeling. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ni1-Cp(c) 1.8120(7), Ni1-C1 2.1836(13), Ni1-C2 2.1736(13), Ni1-C3 2.1639(13), Ni1-C4 2.1710(13), Ni1-C5 2.1949(13), Cp(c)1-Ni1-Cp(c)2 179.991(1).

groups in **2-Me** are sited *anti* to each other with respect to the  $(\eta^{5}-C_{5}H_{4}Me)\cdots Ni\cdots(\eta^{5}-C_{5}H_{4}Me)$  vector, and the Ni–cyclopentadienyl centroid distance is 1.8120(7) Å. The mean Ni–C distance in **2-Me** is 2.1774(13) Å, which corresponds well with the analogous Ni–C bonds in [Ni( $\eta^{5}-C_{5}H_{5}$ )] (mean: 2.178(4) Å), despite the variation in the cyclopentadienyl ligand.<sup>26</sup>

Synthesis of Ni Chlorotrialkylphosphine Cyclopentadienyl Complexes 3-R, 4, and 5. With a range of Niphosphine and nickelocene complexes in hand, we attempted the synthesis of different Ni(II) chlorotrialkylphosphine cyclopentadienyl complexes as precursors for the Ni-Ni dimeric complexes. Only one such Ni complex,  $[Ni(Cl)(\eta^{5}-C_{5}H_{5})(PEt_{3})]$  (3-Et), had been previously reported, and thus



Figure 4. Solid state structures of complexes (a) 3-Me at 90 K, (b) 3-"Pr at 150 K, and (c) 3-"Bu at 90 K with selective labeling. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity.



Figure 5. Solid state structures of complexes (a) 4, (b) 5, and (c) 6 all at 90 K with selective labeling. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity.

	2.14	<b>2 F</b> + <sup>22</sup>	2 //D	2 #D	4	~	1
	3-Me	3-Et	3-"Pr	3-"Bu	4	5	0
Ni-P	2.1612(10)	2.1505(3)	2.1529(4)	2.1412(5)	2.1446(8)	2.1441(10)	2.1600(8)
Ni-Cl	2.1834(10)	2.1871(3)	2.1826(5)	2.1973(5)	2.1930(8)	2.1921(10)	2.2299(7)
Ni–Cp(c)	1.7476(16)	1.753(8)	1.7560(9)	1.7490(10)	1.7461(14)	1.7444(16)	1.7477(13)
P-Ni-Cp(c)	132.83(7)	137.5(3)	133.45(4)	134.07(4)	133.12(5)	133.93(6)	122.71(5)
Cl-Ni-Cp(c)	131.55(7)	130.4(3)	131.84(4)	133.14(4)	132.31(5)	132.98(6)	133.42(5)
P-Ni-Cl	95.56(4)	92.06(5)	94.42(2)	92.68(2)	94.57(3)	92.74(3)	103.40(3)
${}^{a}Cp(c) = centroid at cyclopentadienyl.$							

Table 1. Selected Mean Bond Lengths (Å) and Angles (deg) for Complexes 3-Me, 3-Et, 3-"Pr, 3-"Bu, 4, 5, and 6"

we sought to extend this to a range of different analogues to probe their reactivity in the formation of dimeric Ni complexes.<sup>22</sup> The reaction of nickelocene with the *bis*(trialkylphosphine) Ni-dichlorides **1-Me**, **1-**<sup>*n*</sup>**Pr**, or the literature known analogue **1-**<sup>*n*</sup>**Bu**<sup>20</sup> in refluxing THF afforded the corresponding Ni(II) chlorotrialkylphosphine cyclopentadienyl complexes [Ni(Cl)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PR<sub>3</sub>)] (R = Me, **3-Me**; R = "Pr, **3-**"**Pr**; R = "Bu, **3-**"**Bu**) as red crystalline solids (21, 81, 58% yield, respectively). The solid state structures of **3-Me**, **3-**"**Pr**, and **3-**"**Bu** are illustrated in Figure 4.

In order to probe the effect of substitution on the cyclopentadienyl ligand on the reactivity, the Ni-triethylphosphine complex  $[Ni(Cl)_2(PEt_3)_2]$ , **1-Et**, was reacted with the methyl and SiMe<sub>3</sub> substituted nickelocene derivatives **2-Me** and **2-SiMe<sub>3</sub>** via the same route as before in refluxing THF. The PEt<sub>3</sub> substituted precursors were chosen in order to facilitate better comparison with the literature example **3-Et**.  $[Ni(Cl)(\eta^5-C_5H_4Me)(PEt_3)]$ , **4**, and  $[Ni(Cl)(\eta^5-C_5H_4SiMe_3)-(PEt_3)]$ , **5**, were obtained as red crystalline solids in moderate yield (54% and 30% yield, respectively). The solid state structures of 4 and 5 are illustrated in Figure 5.

X-ray Diffraction Analysis of Ni Chlorotrialkylphosphine Cyclopentadienyl Complexes 3-R, 4, and 5. The metal atoms of 3-Me, 3-"Pr, 3-"Bu, 4, and 5 (Figures 4 and 5) are coordinated in a two-legged piano-stool coordination mode, and each lies in a plane formed by the Cp ring centroid, PR<sub>3</sub> and chloride (sum of bond angles between the Cp ring centroid, PR<sub>3</sub>, and chloride ~  $360^{\circ}$ ), which is in agreement with the previously reported 3-Et.<sup>22</sup> The coordination mode of the cyclopentadienyl ligands is independent of any substituents present, with each being bound to the Ni center in an  $\eta^{5}$ -mode. There is little variation between the Ni–centroid, Ni–P, and Ni–Cl bond distances in each of 3, 4, and 5, despite the variation in ligand environment, and these are in agreement with the previously reported 3-Et (bond lengths and angles are outlined in Table 1).

Spectroscopic Characterization of Ni Chlorotrialkylphosphine Cyclopentadienyl Complexes 3-R, 4, and 5. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectra, a downfield shift of the PR<sub>3</sub> resonances compared to complexes 1-R was observed ( $\delta(3-$ Me) = -11.5 ppm,  $\delta(3^{-n}Pr_3) = 16.0$  ppm,  $\delta(3^{-n}Bu_3) = 17.3$ ppm). This is due to the change in the coordination environment around the Ni atom, which brings the centroid of the cyclopentadienyl ligand at an angle of 131-134° to the phosphine ligand, meaning that there is no ligand directly trans to the phosphine. Thus, the phosphine can donate more strongly compared to complexes 1-R, which leads to less electron density around the phosphorus atom and thus a downfield shift. The resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra for 4 and 5 are 27.6 and 24.9 ppm, respectively. These values are quite similar, which is as expected with both bearing ethyl groups on phosphorus and comparable Ni-P bond lengths. The shifts for 4 and 5 are also in the same range as the literature reported shift for 3-Et (32 ppm).<sup>2</sup>

The UV-vis spectra were collected in toluene for complexes **3-Me**, **3-**<sup>*n*</sup>**Pr**, **3-**<sup>*n*</sup>**Bu**, **4**, and **5**, and all have a maximum extinction coefficient of ~700 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at wavelengths of between 496 and 502 nm. These absorptions are both more intense and at slightly longer wavelengths than the corresponding square planar precursors **1-Me** and **1-**<sup>*n*</sup>**Pr** ( $\varepsilon = ~300 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\lambda = 472-488 \text{ nm}$ ), which can be attributed to the change in coordination geometry from square planar to two-legged piano-stool, as well as the introduction of the cyclopentadienyl ligands.

Synthesis and X-ray Diffraction Analysis of the Tethered Ni Chlorotrialkylphosphine Cyclopentadienyl Complex 6. In order to provide for comparison with a bridged Ni-Ni dimer complex, we additionally prepared  $[Ni(Cl)(\kappa^1-\eta^5-C_5H_4CH_2CH_2P^tBu_2)]$  (6) following the reported procedure as shown in Scheme 2.<sup>23</sup> Since the structure in the solid state had not been determined before, we undertook single crystal X-ray diffraction studies on crystals of 6 grown from a saturated toluene solution. The solid state structure of 6 is shown in Figure 5c. Complex 6 crystallizes as a discrete mononuclear chelated species, adopting a two-legged piano-stool geometry around the Ni atom (sum of bond angles between PR<sub>3</sub>, chloride, and Cp centroid ~  $360^{\circ}$ ). The bond distances are comparable to those in complexes 3-Me, 3-Et, 3-"Pr, 3-"Bu, 4, and 5 (see Table 1); however, as a result of the strained nature of the chelating ligand, the bond angles do differ, with the P-Ni-Cp(c) angle narrowing by  $\sim 10^{\circ}$  $(122.71(5)^{\circ} \text{ compared to } 132.83(7) - 137.5(3)^{\circ})$ , along with the opening of the corresponding P–Ni–Cl angle  $(103.40(3)^{\circ})$ compared to  $92.06(5)-95.56(4)^{\circ}$ ). The Cl-Ni-Cp(c) angle is mostly unchanged, however, and lies just above the standard uncertainty of the range of angles for the other complexes  $(133.42(5)^{\circ}$  for **6** vs the range  $130.4(3)-133.14(4)^{\circ}$ ). The ethylene tether adopts a staggered conformation, and the cyclopentadienyl carbon attached to this tether (C5) also lies closer to the Ni center than the other carbons in the ring  $(Ni1-C5 2.022(3) \text{ Å}, Ni1-C1/2/3/4_{av} 2.167(3) \text{ Å});$  this was also observed in analogous compounds described by Butenschön (e.g.,  $[Ni(Me)(\kappa^1-\eta^5-C_5H_4CH_2CH_2P^tBu_2)]$ , Ni1-C1 2.099(11) Å, Ni1-C2/3/4/5<sub>av</sub> 2.125(11) Å).<sup>23</sup>

Synthesis of the Dimeric Ni Cyclopentadienyl Phosphino Complexes 7-R and 8. The synthesis of the dimeric formally Ni(I) complexes was achieved by reduction of the monomeric Ni(II) complexes. The identity of the reducing agent is vitally important, as most, more common, reducing agents, such as alkali metals or KC<sub>8</sub> are too reducing, resulting in over-reduction and intractable products. However, activated

Mg yields the formal Ni(I) complexes. Each of the monomeric complexes 3-Me, 3-"Pr, 3-"Bu, 4, 5, and 6 was reacted with activated Mg in attempts to prepare formal Ni(I)-Ni(I) species of the general form  $[{Ni(\eta^5-C_5H_4R')(PR_3)}_2]$ . In all reactions, a slow color change to dark green was observed. In the cases of 3-Me, 3-<sup>n</sup>Pr, and 6, we were able to successfully isolate the Ni-Ni dimers  $[{Ni(\eta^5-C_5H_5)(PMe_3)}_2]$ , 7-Me (53%),  $[{Ni(\eta^5-C_5H_5)(PMe_3)}_2]$  $C_5H_5)(P^nPr_3)_2$ , 7-"Pr (80%), and [{Ni( $\mu$ : $\eta$ <sup>5</sup>- $C_5H_4CH_2CH_2P(^{t}Bu)_2)_2$ ], 8 (<1%), respectively. Unfortunately, from the reactions of 3-"Bu, 4, or 5 with activated Mg, only intractable mixtures were obtained, and attempts to crystallize any reaction products led to further decomposition. The successful isolation of the dimeric complexes with both phosphine and cyclopentadienyl-based ligands thus seems to be much more sensitive to the substitution patterns of the cyclopentadienyl ligands than that of the phosphines. This is in contrast to the observation by Figueroa and co-workers of the steric bulk of the L-donor isocyanide ligand determining the structure.<sup>19</sup> The steric demands of the phosphine ligands do not seem to play a major role in the successful preparation of the dimeric species, contrasting the assumptions made in the work by Wilke and co-workers.<sup>18</sup> Inspection of the Tolman cone angles reveals that, depending on how exactly the values are calculated (original Tolman/for tetrahedral Ni complex), PEt<sub>3</sub>, P<sup>n</sup>Pr<sub>3</sub>, PPh<sub>3</sub>, and P<sup>n</sup>Bu<sub>3</sub> all have a very similar steric demands:  $PEt_3$  (132°/169°),  $P''Pr_3$  (132°/169°),  $PPh_3$  (145°/ 166°), and  $P''Bu_3$  (132°/172°).<sup>28</sup> Thus, the unsuccessful isolation of 7-"Bu and 7-Ph cannot be attributed to steric effects alone. This demonstrates how crucial the choice of alkyl substituent on the phosphine ligand is for the formation of Ni-Ni complexes.

NMR Spectroscopic Characterization of Dimeric Ni **Complexes 7-R.** The  ${}^{31}P{}^{1}H{}$  NMR resonances for the PR<sub>3</sub> substituents in 7-R are very close to those observed for the monomeric precursor complexes 3-R, with -10.1 ppm for 7-Me and 18.0 ppm for 7-"Pr. This signifies an upfield shift of 1.4 and 1.3 ppm, respectively. The <sup>31</sup>P{<sup>1</sup>H} NMR resonance for 7-Et was reported to be at 26.9 ppm, which is a 3.3 ppm shift upfield compared to the monomeric 3-Et.<sup>18,22</sup> The resonances for 7-Me, 7-Et, and 7-"Pr follow the trend expected from the free alkylphosphine ligands with 7-Me being the furthest upfield, followed by 7-"Pr approximately 30 ppm downfield and 7-Et shifted another 9 ppm downfield. For reduction of the Ni atoms from +II to +I, a larger change in chemical shift might be reasonably anticipated, as the P atom might be donating less electron density to the Ni ion in the reduced complexes. However, the trend towards more upfield resonances corresponds well to the increased electron density on P. The smaller change in chemical shift compared to the differences between 1-R and 3-R can be rationalized by the smaller changes in the coordination geometry around the Ni atom with the P-Ni-Cp(c) angle opening up by only 10° when going from 3-R to 7-R, as opposed to  $40^{\circ}$  from 1-R to 3-R

X-ray Diffraction Analysis of Dimeric Ni Complexes 7-R and 8. The solid state structures of 7-"Pr and 8 are illustrated in Figure 6. The solid state structure of 7-Me is shown in the Supporting Information (Figure S1). The X-ray data obtained for 7-Me were of poor quality, so reliable analysis of the metrical parameters of the complex is not possible but the connectivity is clear and confirms the formulation of 7-Me to be analogous to that of 7-"Pr. Complexes 7-Me and 7-"Pr adopt geometries akin to that of 7-



Figure 6. Solid state structures of complexes (a) 7-<sup>*n*</sup>Pr and (b) 8 at 150 K with selective labeling. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity.

Et,<sup>22</sup> with the cyclopentadienyl rings adopting an  $\eta^5$  binding mode. This contrasts to  $[{Pd(Cp)(PMe_3)}_2]$ , reported by Werner and co-workers, in which the cyclopentadienyl ligands behave like allylic fragments, adopting a bridging conformation.<sup>29,30</sup> The difference in binding mode can be attributed to the relative size of the metals (Ni 3d 1.10 Å *vs* Pd 4d 1.20 Å).<sup>31</sup> The Ni centers in 7-*"*Pr are coordinated in two-legged pianostool fashion, though the bond distances and angles vary to that reported for 7-Et, with slightly shorter Ni–Ni and Ni-Cp(c) distances and smaller P–Ni–Ni and Cp(c)–Ni–Ni angles. These are detailed in Table 2. The torsion angles P– Ni–Ni–P are quite similar to 100.84(8)° for 7-Et and 103.66(4)° for 7-*"*Pr. The slightly larger angle for 7-*"*Pr can be explained by the higher steric demand of the "Pr substituents on the phosphine ligands compared to the ethyl groups in 7-Et.

In both unbridged Ni-Ni complexes 7-Me and 7-"Pr, the substituents are in a *cis* arrangement, as previously observed for the ethyl substituted analogue reported by Wilke.<sup>18</sup> The bridging ligand in 8 changes this to a *trans* arrangement. A comparison of the Ni–Ni interactions reveals that the tethered environment has imposed a not inconsiderable lengthening of ~0.2 Å to the Ni–Ni bond in 8 compared to 7-Et and 7-"Pr (see Table 2). The unbridged Ni–Ni bond in 7-"Pr is also slightly shorter than the reported distance of 2.407(1) Å for 7-Et.<sup>18</sup> The elongation of the bond in 8 with otherwise similar substituents is most likely due to the bridging ligand leading to steric hindrance.

The structure of **8** retains a two-legged piano-stool coordination geometry around the Ni centers (sum of bond angles between  $PR_3$ , other Ni, and Cp centroid ~ 360°). The cyclopentadienyl centroid bond distances are slightly longer in the dinuclear structure than in the precursor Ni(II) complex **6**, resulting from the slightly larger size of the formal Ni(I) ion. The coordination geometry is altered from that of the untethered analogue as a result of the ethylene linkage imposing steric constraints upon the relative positions of the coordinated fragments of the ligand. Accordingly, the P–Ni–Ni angle is enlarged in comparison to that of 7-Et and 7-"Pr, as is the torsion angle P–Ni–Ni–P.

Trends in the Experimental Characterization Data. Table 3 summarizes the key spectroscopic and crystallographic data for the synthesized complexes. Several trends can be observed in the spectroscopic and crystallographic data. The observed resonances in the  ${}^{31}P{}^{1}H$  NMR are shifted increasingly downfield with each complex along the reaction sequence, starting from the Ni(II) dichloro diphosphine complexes  $[Ni(Cl)_2(PR_3)_2]$  1-R, followed by the Ni(II) chlorotrialkylphosphine cyclopentadienyl complexes [Ni(Cl)- $(\eta^5 - C_5 H_4 R')(PR_3)$ ] 3-R/4/5, going to the resulting formal Ni(I) cyclopentadienyl phosphino dimers [{Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)- $(PR_3)_{2}$  7-R. This observation can be explained by the increasing donation of electron density by the phosphine ligand to the nickel atom. Simultaneously, the Ni-P bond lengths decrease throughout the sequence, also indicating a strengthening of the Ni-P bond. The largest changes in both <sup>31</sup>P{<sup>1</sup>H} NMR resonances as well as Ni–P bond lengths are observed when introducing the cyclopentadiene ligands, which can be attributed to the change in coordination environment around the nickel atoms. Similarly, the maximum absorption in the UV-vis spectra changes significantly between the nickelocene complexes 2-R and the Ni(II) chlorotrialkylphosphine

Table 2. Selected Mean Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for the Dimeric Complexes 7-Et,<sup>18</sup> 7-"Pr, and 8

	7-Et <sup>18</sup>	7-"Pr	8
Ni-Ni	2.407(1)	2.3931(6)	2.6027(17)
Ni-P	2.122(1)	2.1228(9)	2.1649(19)
Ni-Cp(c)	1.7935(18)	1.7814(17)	1.790(4)
Ni-C	2.105(3) - 2.166(4)	2.101(3)-2.171(4)	2.116(7)-2.191(7)
P-Ni-Cp(c)	140.68(11)	139.81(8)	142.00(14)
P-Ni-Ni	92.89(7)	91.99(3)	101.22(7)
Cp(c)–Ni–Ni	126.25(7)	126.72(7)	116.38(13)
P-Ni-Ni-P	100.84(8)	103.66(4)	121.25(8)

	$^{31}P{^{1}H} NMR$	UV-vis	bond lengths (Å)		
compound	$\delta$ (ppm)	$\lambda_{\max}$ (nm)	Ni-P	Ni-Cp(c)	Ni-Ni
1-Me	-23.1	472	2.2263(6)		
1-"Pr	-3.2	488	2.2293(6)		
2-Me		679		1.8120(7)	
2-SiMe <sub>3</sub>		697			
3-Me	-11.5	497	2.1612(10)	1.7476(16)	
3-"Pr	16	502	2.1529 (4)	1.7560(9)	
3-"Bu	17.3	502	2.1412(5)	1.7490(10)	
4	27.6	496	2.1446(8)	1.7461(14)	
5	24.9	501	2.1441(10)	1.7444(16)	
7-"Pr	18		2.1228(9)	1.7814(17)	2.3931(6)
7-Me	-10.1				
8			2.1649(19)	1.790(4)	2.6027(17)

Tab	le 3.	Selec	ted S	Spectroscopic and	Crystal	lographic	Data	for Al	l New	Complexes	s
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cyclopentadienyl complexes 3-R, 4, and 5. In contrast, the dimerization only leads to small shifts in the observed  ${}^{31}P{}^{1}H{}$ NMR resonances and bond metrics, due to the coordination environment around nickel not changing much. Looking at the same types of complexes (for example, 3-R) with different alkyl groups on the phosphine ligand, a clear trend can be observed for the resonances in the  ${}^{31}P{}^{1}H{}$  NMR spectra. The resonances are shifted downfield when going from methyl to *n*-propyl to *n*-butyl. This trend is also observed for the free PR<sub>3</sub> ligands and rationalized by the increasing negative inductive effect of alkyl groups on phosphorus. The second influence on the observed  ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$  NMR resonances stems from the coordination to Ni and can be observed in the Ni-P bond lengths. These decrease slightly going from 3-Me (2.1612(10) Å) to 3-"Pr (2.1529(4) Å) and 3-"Bu (2.1412(5) Å), showing the strengthening of the Ni-P bonds associated with increasing donation of electron density from the phosphine ligands to Ni.

**Density Functional Theory Calculations on Dimeric** Ni Complexes 7-R and 8. In order to gain more insight into the Ni-Ni bonding situation, we performed DFT calculations on compounds 7-Me, 7-"Pr, and 8. The bond lengths and angles of the optimized geometries match well with the structures in the solid state with experimental solid state vs computed gas-phase deviations in the range of 0.03 Å and 0.4°, respectively. The Ni-Ni bond length in 7-Me (2.4193 Å) is calculated to be very similar to that of 7-"Pr (2.4257 Å). The same holds true for the Ni-P and P-C bond lengths, enabling the assumption that the calculated structures are qualitatively representative of the experimental solid state structures. In addition to the dimers 7-Me and 7-"Pr with the phosphine ligands in a cis arrangement, the trans isomers were optimized for comparison. For 7-<sup>*n*</sup>**Pr**, a minimum structure with a *trans* configuration of the ligands could be found, albeit 69 kJ/mol higher in energy. This large energy difference explains the sole observation of the cis isomer in the experiments. The optimization of trans-7-Me leads to cis-7-Me, which can be attributed to less steric hindrance between the ligands in the cis configuration compared to a trans arrangement. Consequently, the Ni-Ni bond length is shorter in the cis complexes, enabling better orbital overlap and stabilization of the Ni-Ni bond. The same reasoning can be applied to 7-"Pr, where the Ni-Ni bond length in the trans isomer is elongated to 2.7075 Å (*cis*: 2.4257 Å) and the complex is destabilized by 69 kJ/mol.

Charges for the Ni atoms were calculated with different methods and are given in Table  $4^{32-34}$  Due to the different

Table 4. Computed Charges for the Nickel Atoms and Nalewajski–Mrozek Bond Orders for the Nickel–Nickel Bonds in 7-Me, 7-"Pr, and 8

	charge on Ni			
	NBO	Hirshfeld	MDC-q	Nalewajski–Mrozek bond order for Ni–Ni
7-Me	0.37	0.15	-0.03	0.45
7- <sup>n</sup> Pr	0.38	0.15	0.05	0.45
8	0.43	0.16	0.02	0.44

approaches in defining the atoms in a molecule and calculations of the charge, the values differ, but most importantly produce a consistent overall trend. The calculated charges on the Ni atoms are as expected rather small with little deviation between the complexes. For the Ni atom, NBO charges are in the range of 0.37-0.43, Hirshfeld charges are 0.15-0.16, and MDC-q charges are between -0.03 and 0.05. Thus, the Ni atom in these complexes can be described with the formal low oxidation state of +I. For further characterization of the nature of the Ni-Ni bond, Nalewajski-Mrozek bond orders were calculated. These are basis set independent and have been shown to correlate well with experimental data for transition metal complexes.<sup>35</sup> The calculated bond orders of 0.44 for 8 and 0.45 for 7-Me and 7-"Pr support the description of the Ni-Ni bonds as single bonds with significant ionic contribution, where a charge-shift nature may be operating (see below). The slightly lower bond order for the bridged complex was expected due to the elongated Ni-Ni bond length, which is implied by the sterics of the bridging ligand.

A topological analysis of the electron density was performed with the Quantum Theory of Atoms in Molecules (QTAIM).<sup>36</sup> The QTAIM analysis found bond paths and bond critical points (BCPs) between the nickel atoms in all three complexes. At the BCP, several parameters are informative of the nature of the bond: The electron density  $\rho(\mathbf{r})$  shows a minimum at the BCP. The Laplacian  $\nabla^2 \rho(\mathbf{r})$  is negative for covalent bonds, but can be positive, for example, for closed-shell and ionic interactions. Another insightful value is the electronic energy density  $H(\mathbf{r})$ , which is the sum of the kinetic and potential energy:  $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$ . The energy density  $H(\mathbf{r})$  is negative for covalent bonds and positive for ionic bonds, H bonds, and van der Waals bonds.<sup>37</sup> A summary of the results obtained from a QTAIM analysis of complexes 7-Me, 7-"Pr, and 8 can be found in Table 5. The Laplacians of

Table 5. Values for the Electron Density  $\rho(\mathbf{r})$ , the Laplacian  $\nabla^2 \rho(\mathbf{r})$ , and Electronic Energy Density  $H(\mathbf{r})$  at the Ni–Ni BCPs for 7-Me, 7-"Pr, and 8

	$ ho(\mathbf{r})$	$ abla^2 ho({f r})$	$H(\mathbf{r})$	ε
7-Me	0.051	0.069	-0.012	0.027
7-"Pr	0.051	0.051	-0.012	0.017
8	0.039	0.035	-0.009	0.023

the electron density are positive, but close to zero and in the range of mainly ionic bonds for all three complexes (0.07 for 7-Me, 0.05 for 7-"Pr, and 0.04 for 8).<sup>38-41</sup> The electronic energy density  $H(\mathbf{r})$  was found to be -0.012 for 7-Me and 7-<sup>n</sup>Pr and -0.009 for 8, suggesting a small amount of covalent bonding. These values indicating an ambiguity between ionic and covalent bonding are very typical for metal-metal bonds and have recently been shown to be possibly best described as charge-shift bonds.<sup>42</sup> The bond ellipticity  $\hat{\varepsilon}$  at the bond critical points of 0.02-0.03 is close to zero in all three complexes, which corresponds well with a bond of mainly  $\sigma$ -character between the nickel atoms. The lower values for  $\rho(\mathbf{r})$ ,  $\nabla^2 \rho(\mathbf{r})$ , and  $H(\mathbf{r})$  for 8 compared to 7-Me and 7-<sup>*n*</sup>Pr confirm the lower Ni-Ni bond order and an overall weaker Ni-Ni bond in 8. This is in line with the observed elongated Ni-Ni bond length, which is caused by the steric strain of the bridging ligand.

Inspection of the molecular orbitals shows that the main contribution to the nickel-nickel bond for all three complexes is a  $\sigma$ -bonding orbital which is mainly formed by metal dorbitals (Figure 7). In 7-Me, both Ni atoms contribute similarly to the MO (47.3% and 45.9%). The main contributions come from the  $d_{x^2-y^2}$  orbitals with 20.7% and 15.7% for the two Ni ions, respectively, and the Ni1  $d_{z^2}$ (13.0%) and Ni2  $d_{xy}$  orbitals (13.9%). Similar contributions to the  $\sigma$ -bonding MO are obtained for 7-<sup>*n*</sup>Pr with 46.4% and 45.6% contribution for the two Ni atoms. The main contributions are from  $d_{xz}$  (29.9%) and  $d_{z^2}$  (11.1%) orbitals for Ni1 and from  $d_{yz}$  (28.1%) and  $d_{z^2}$  (11.3%) for Ni2. As expected from inspection of the molecular orbitals, the contributions to the HOMO-8 are again similar for 8: Ni1 contributes 47.1%, where 14.9% are from the  $d_{xy}$  orbital, 12.3% from the  $d_{x^2-y^2}$  and 11.4% from the  $d_{yz}$  orbital. Ni2 contributes 44.5%, with 23.2% from the  $d_{x^2-y^2}$  and 9.2% from the  $d_{z^2}$ . No interaction was found between the ligands of the two Ni fragments and the Ni-Ni bonds in 7-Me and 7-"Pr, confirming the unbridged nature of those Ni-Ni bonds. In each case, the LUMO of these complexes represents a Ni-Ni  $\sigma^*$  MO, which nicely accounts for the fact that 2-electron

reduction of these dimers would be expected to result in annihilation of the Ni–Ni bonds and formation of monomeric  $[Ni(Cp)(PR_3)]^{1-}$  18-electron anions that are analogous to the  $[Fe(Cp)(CO)_2]^{1-}$  anion.

## SUMMARY AND CONCLUSIONS

A modular approach for the preparation of new Ni-Ni complexes was investigated. We were able to synthesize a library of Ni complexes with different phosphine and substituted cyclopentadienyl ligands. In the first step, Ni complexes  $[Ni(Cl)_2(PR_3)_2]$  (1-Me, R = Me; 1-<sup>*n*</sup>Pr, R = <sup>*n*</sup>Pr; **1-**<sup>*n*</sup>**Bu**, R = <sup>*n*</sup>Bu) and nickelocene complexes  $[Ni(\eta^5 - C_5H_4R')_2]$ with R' = H (2-H), Me (2-Me), and SiMe<sub>3</sub> (2-SiMe<sub>3</sub>) were synthesized. From these, Ni chloro cyclopentadienyl phosphine complexes [NiCl(PR<sub>3</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R')] (**3-Me**, R = Me, R' = H;  $3^{-n}Bu$ , R= <sup>*n*</sup>Bu, R' = H;  $3^{-n}Pr$ , R = <sup>*n*</sup>Pr, R' = H; 4, R = Et, R' = Me; 5, R = Et,  $R' = SiMe_3$ ) were synthesized via a ligand exchange route. Reduction of these monomeric Ni complexes with activated Mg resulted in dimerization and formation of Ni-Ni complexes. Complexes  $[{Ni(\eta^5-C_5H_5)(PR_3)}_2]$  (7-Me and 7-<sup>*n*</sup>Pr) could be isolated and characterized spectroscopically and by single crystal X-ray crystallography. These two dimeric species contain very rare unbridged Ni-Ni bonds, adding two more examples to only three previously known ones. So far, only two other examples with cyclopentadienyl and phosphine or isocyanide ligands had been known, whereas the other known Ni-Ni species contained solely cyanide ligands and is therefore difficult to adapt for further applications. The systematic variation of the substituents on the phosphine and cyclopentadienyl ligands allowed for insights into the influence of the ligands on the dimer formation and the Ni-Ni bond properties to be probed. It was shown that the previously assumed steric effects (as also observed in isocyanide complexes) seem to be rather negligible for the phosphines, as 7-"Pr could be isolated successfully, but the sterically very similar 7-"Bu could not be isolated. DFT calculations show the Ni-Ni bonding interaction in the dimeric complexes to be of  $\sigma$ -type, and possibly exhibiting charge-shift character. No interactions between the ligands were found, which confirms the unbridged nature of the Ni-Ni bonds. Additionally, the bridged Ni-Ni complex [{Ni( $\mu$ : $\eta^5$ - $C_5H_4CH_2CH_2P(^tBu)_2)_2$  (8) was synthesized from the monomeric precursor  $[Ni(Cl)(\kappa^1-\eta^5-C_5H_4CH_2CH_2P^tBu_2)]$ (6) to allow for direct comparison of the Ni-Ni bonds between the bridged dimer 8 and the unbridged dimers 7-Me and 7-"Pr. The bridging ligand in 8 leads to an elongated Ni-



Figure 7. HOMO-8 of (a) 7-Me, (b) 7-Pr, and (c) 8 showing the Ni-Ni  $\sigma$ -bonds. H atoms are omitted for clarity. Contour level set to 0.05.

Ni bond distance, as well as an enlarged P–Ni–Ni–P torsion angle compared to 7-Me and 7-"Pr. Bonding analysis of the Ni–Ni bond in 8 reveals the bond to be slightly weaker than in 7-Me and 7-"Pr, which can be accredited to the steric strain imposed by the tethering ligand. The Ni-Ni complexes disclosed here could be employed as starting materials for hetero-bimetallic complexes or larger cluster molecules.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out using Schlenk techniques, or in an MBraun Unilab glove box, under an atmosphere of dry and oxygen-free dinitrogen. Tetrahydrofuran (THF), diethyl ether, *iso*-hexane, pentane, and toluene were dried by passage through activated alumina and degassed before use. Methylcyclohexane was distilled under dinitrogen from K. All solvents were stored over K-mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated benzene was distilled from K, degassed by three freeze-pump-thaw cycles and stored under dinitrogen. The compounds  $[Ni(Cl)_2(PEt_3)_2]^{,20}$   $[Ni-(Cl)_2(P^nBu_3)_2]^{,20}$   $[Ni(\eta^5-C_5H_5)_2]^{,21}$   $[Ni(NH_3)_6]Cl_2^{,21}$   $[Na(\eta^5-C_5H_4Me)]^{,43}$   $[K(\eta^5-C_5H_4TMS)]^{,44}$   $[Ni(Cl)(\eta^5-C_5H_5)(PEt_3)]^{,18}$  spiro[4.2]hepta-1,3-diene, <sup>45</sup>  $[Ni(Cl)(\kappa^1:{(\eta^5-C_5H_4)(CH_2)_2}) P({}^{t}Bu)_2]^{,23}$  and activated Mg<sup>46</sup> were prepared according to literature procedures. All other reagents were used as received.

<sup>1</sup> <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.1, 100.1, and 162.0 MHz, respectively; chemical shifts are quoted in ppm and are relative to Me<sub>4</sub>Si or external 85% H<sub>3</sub>PO<sub>4</sub>. FTIR spectra were recorded on a Bruker tensor 27 spectrometer in Nujol, and absorptions are reported in inverse centimeters as w (weak), m (medium), or s (strong). UV/ vis spectra were recorded in a 10 mm quartz cell on a Perkin Elmer Lambda 750 UV/VIS/NIR Spectrometer. Elemental microanalyses were carried out by Mr. Stephen Boyer (London Metropolitan University), or Mr. Mark Jennings (University of Manchester).

**Preparation of [Ni(Cl)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (1-Me).** Trimethylphosphine (20 mL, 20.00 mmol, 1.0 M in THF) was added to a stirring slurry of anhydrous NiCl<sub>2</sub> (1.35 g, 10.42 mmol) in THF (50 mL) at room temperature. The resulting blue mixture was refluxed at 90 °C for 20 h. After this time, the resulting red solution was allowed to cool to room temperature, volatiles were removed *in vacuo*, and the resulting oily red residue was extracted into pentane (20 mL). The solution was stored at -30 °C for 24 h to afford **1-Me** as red blocks. Yield: 2.20 g, 75%. Anal. Calcd for C<sub>6</sub>H<sub>18</sub>Cl<sub>2</sub>NiP<sub>2</sub>: C, 25.58; H, 6.44; N, 0.00%. Found: C, 25.70; H, 6.55; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 1.04 (18H, s, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 11.51 (s, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) -23.1. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 672 (w), 704 (w), 945 (w), 1409 (m), 1626 (m). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (472 nm),  $\varepsilon = 268$  dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)<sub>2</sub>(P<sup>P</sup>Pr<sub>3</sub>)<sub>2</sub>] (1-<sup>***n***</sup>Pr). Tripropylphosphine (3 mL, 15.00 mmol) was added to a stirring slurry of anhydrous NiCl<sub>2</sub> (0.98 g, 7.56 mmol) in THF (50 mL) at room temperature, and the reaction mixture was refluxed at 90 °C for 20 h. After this time, the resulting red solution was allowed to cool to room temperature, volatiles were removed** *in vacuo***, and the resulting oily red residue was extracted into hexane (20 mL). The solution was stored at -30 °C for 24 h to afford 1-<sup>***n***</sup>Pr as red blocks. Yield: 1.96 g, 58%. Anal. Calcd for C<sub>18</sub>H<sub>42</sub>Cl<sub>2</sub>NiP<sub>2</sub>: C, 48.04; H, 9.41; N, 0.00%. Found: C, 47.85; H, 9.30; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 1.15 (18H, t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, CH<sub>3</sub>), 1.66 (12H, m, CH<sub>2</sub>), 1.85 (12H, m, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) -3.2. FTIR (Nujol): \tilde{v} (cm<sup>-1</sup>) 660 (w), 1076 (s), 1414 (w). UV/vis (Toluene, 295 K): λ<sub>max</sub> (488 nm), \varepsilon = 381 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.** 

**Preparation of [Ni**( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>] (2-Me). [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (2.80 g, 12.08 mmol) was added to a solution of [Na( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)] (2.48 g, 24.31 mmol) in THF (75 mL), and the reaction mixture was stirred for 18 h at room temperature. After this time, volatiles were removed *in vacuo*, giving a brown solid which was purified by sublimation, yielding green blocks of 2-Me. Yield: 0.61 g, 23%. Anal. Calcd for

C<sub>12</sub>H<sub>14</sub>Ni: C, 66.44; H, 6.50; N, 0.00%. Found: C, 66.21; H, 6.35; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.42 (s, CH<sub>3</sub>). No signal could be observed for the C<sub>5</sub>H<sub>4</sub> protons. Due to poor solubility, no <sup>13</sup>C{<sup>1</sup>H} NMR could be obtained. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 768 (w), 776 (m), 929 (w), 1402 (w), 2729 (w). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (679 nm),  $\varepsilon = 64$  dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>] (2-SiMe<sub>3</sub>).** [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (3.46 g, 14.92 mmol) was added to a solution of [K(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)] (5.28 g, 29.93 mmol) in THF (75 mL), and the reaction mixture was gently heated to 60 °C for 5 h. After this time, volatiles were removed *in vacuo* and the product was extracted into hexane (20 mL). Volatiles were removed *in vacuo* from the mother liquor, yielding **2-SiMe**<sub>3</sub> as a dark green oil. Yield: 1.56 g, 31 %. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>NiSi<sub>2</sub>: C, 57.67; H, 7.86; N, 0.00%. Found: C, 57.83; H, 7.78; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.37 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.19(2H, m, C<sub>5</sub>H<sub>4</sub>), 1.52 (2H, m, C<sub>5</sub>H<sub>4</sub>). Due to poor solubility, no <sup>13</sup>C{<sup>1</sup>H} NMR could be obtained. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 774 (m), 1005 (m), 1542 (m), 2342 (w). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (697 nm),  $\varepsilon$  = 94 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)**( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(**PMe<sub>3</sub>**)] (3-Me). THF (50 mL) was added to a stirring mixture of 1-Me (2.18 g, 7.74 mmol) and 2-H (1.48 g, 7.84 mmol). The reaction mixture was refluxed at 90 °C for 30 h. After this time, the resulting dark red solution was allowed to cool to room temperature, filtered, and volatiles were removed *in vacuo*. The resulting red solid was extracted into toluene (20 mL), and the solution was cooled to -30 °C for 24 h to afford 3-Me as red blocks. Yield: 0.75 g, 21%. Anal. Calcd for C<sub>8</sub>H<sub>14</sub>ClNiP: C, 40.83; H, 6.00; N, 0.00 %. Found: C, 40.98; H, 6.11; N, 0.00 %. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.95 (9H, d, <sup>2</sup>J<sub>HP</sub> = 10.8 Hz, CH<sub>3</sub>), 5.12 (5H, s, C<sub>5</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 16.06 (d, J<sub>CP</sub> = 30.2 Hz, CH<sub>3</sub>), 91.95 (d, J<sub>CP</sub> = 2.0 Hz, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) -11.5. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 676 (w), 853 (w), 953 (m), 1284 (w). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (497 nm),  $\varepsilon$  = 750 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)**( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(P<sup>n</sup>Pr<sub>3</sub>)] (3-<sup>n</sup>Pr). THF (50 mL) was added to a stirring mixture of 1-<sup>n</sup>Pr (1.96 g, 4.35 mmol) and 2-H (0.89 g, 4.71 mmol). The reaction mixture was refluxed at 90 °C for 20 h. After this time, the dark red solution was allowed to cool to room temperature, filtered, and volatiles were removed *in vacuo*. The resulting red solid was extracted into hexane (20 mL), and the solution was stored at room temperature for 24 h to afford 3-<sup>n</sup>Pr as red plates. Yield: 2.24 g, 81%. Anal. Calcd for C<sub>14</sub>H<sub>26</sub>ClNiP: C, 52.63; H, 8.20; N, 0.00%. Found: C, 52.59; H, 8.30; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.99 (9H, t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, CH<sub>3</sub>), 1.36 (6H, m, CH<sub>2</sub>), 1.58 (6H, m, CH<sub>2</sub>), 5.17 (5H, s, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 15.78 (d, J<sub>CP</sub> = 14.1 Hz, CH<sub>2</sub>), 17.93 (s, CH<sub>3</sub>), 26.73 (d, <sup>2</sup>J<sub>CP</sub> = 27.0 Hz, CH<sub>2</sub>), 91.91 (d, J<sub>CP</sub> = 2.0 Hz, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 160. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 775 (w), 1218 (w), 1402 (m), 1946 (w), 2029 (w). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (502 nm),  $\varepsilon = _{737}$  dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)**( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $P^n$ Bu<sub>3</sub>)] (3-<sup>*n*</sup>Bu). THF (50 mL) was added to a stirring mixture of 1-<sup>*n*</sup>Bu (1.20 g, 2.25 mmol) and 2-H (0.44 g, 2.33 mmol). The reaction mixture was refluxed at 90 °C for 21 h. After this time, volatiles were removed *in vacuo* and the resulting red oil was extracted into hexane (20 mL). The solution was cooled to -30 °C for 24 h to afford 3-<sup>*n*</sup>Bu as red plates. Yield: 1.27 g, 58 %. Anal. Calcd for C<sub>17</sub>H<sub>32</sub>ClNiP: C, 56.47; H, 8.92; N, 0.00%. Found: C, 56.36; H, 9.05; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.98 (9H, t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, CH<sub>3</sub>), 1.46 (12H, m, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, CH<sub>2</sub>), 1.62 (6H, m, CH<sub>2</sub>), 5.21 (5H, s, C<sub>3</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 13.68 (d, <sup>2</sup>J<sub>CP</sub> = 14.1 Hz, CH<sub>2</sub>), 24.14 (s, CH<sub>3</sub>), 24.29 (d, J<sub>CP</sub> = 27.0 Hz, CH<sub>2</sub>), 91.94 (d, J<sub>CP</sub> = 2.0 Hz, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 17.3. FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 609 (w), 890 (w), 905 (w), 1403 (m), 3131 (w, br). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (502 nm),  $\varepsilon$  = 740 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)**( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)(PEt<sub>3</sub>)] (4). THF (50 mL) was added to a stirring mixture of 1-Et (0.69 g, 1.89 mmol) and 2-Me (0.42 g, 1.94 mmol). The reaction mixture was refluxed at 90 °C for 20 h. After this time, the resulting dark red solution was allowed to cool to room temperature, filtered, and volatiles were removed *in* 

*vacuo*. The resulting red solid was extracted into toluene (10 mL). The solution was cooled to -30 °C for 24 h to afford 4 as red blocks. Yield: 0.57 g, 54%. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>ClNiP: C, 49.46; H, 7.61; N, 0.00%. Found: C, 49.61; H, 7.68; N, 0.00%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K):  $\delta$  (ppm) 1.02 (9H, m, CH<sub>3</sub>), 1.31 (6H, m, CH<sub>2</sub>), 1.71 (3H, d, <sup>4</sup>J<sub>HH</sub> = 3.6 Hz, C<sub>5</sub>H<sub>4</sub>Me), 4.26 (6H, q, <sup>3</sup>J<sub>HH</sub> = 2.0 Hz, CH<sub>2</sub>), 5.57 (4H, m, br, C<sub>5</sub>H<sub>4</sub>Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K):  $\delta$  (ppm) 7.96 (s, CH<sub>3</sub>), 13.46 (s, CH<sub>3</sub>), 16.76 (d, J<sub>CP</sub> = 17.1 Hz, CH<sub>2</sub>), 80.72 (C<sub>5</sub>H<sub>4</sub>Me), 98.98 (s, C<sub>5</sub>H<sub>4</sub>Me), 113.58 (s, C<sub>q</sub>-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K):  $\delta$  (ppm) 27.6 (m, br). FTIR (Nujol):  $\tilde{v}$  (cm<sup>-1</sup>) 768 (m), 917 (w), 1351 (m), 1416 (w), 2341 (w), 2360 (w). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (496 nm),  $\varepsilon$  = 1018 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of [Ni(Cl)**( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>TMS)(PEt<sub>3</sub>)] (5). THF (50 mL) was added to a stirring mixture of 1-Et (1.46 g, 3.99 mmol) and 2-SiMe<sub>3</sub> (1.16 g, 3.48 mmol). The reaction mixture was refluxed at 90 °C for 20 h. After this time, the resulting dark red solution was allowed to cool to room temperature, filtered, and volatiles were removed *in vacuo*. The resulting red solid was extracted into methylcyclohexane (10 mL). The solution was cooled to 9 °C for 24 h, affording 5 as red needles. Yield: 0.62 g, 30%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.56 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.02 (9H, m, br, CH<sub>3</sub>), 1.28 (6H, m, br, CH<sub>2</sub>), 5.12 (4H, m, C<sub>5</sub>H<sub>4</sub>Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) -0.17 (s, Si-(CH<sub>3</sub>)<sub>3</sub>), 7.97 (s, CH<sub>3</sub>), 16.50 (d, J<sub>CP</sub> = 14.1 Hz, CH<sub>2</sub>), 91.37 (s, C<sub>5</sub>H<sub>4</sub>), 91.78 (s, C<sub>q</sub>), 95.8 (d, J<sub>CP</sub> = 5.1 Hz, C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 24.9 (br). UV/vis (Toluene, 295 K):  $\lambda_{max}$  (501 nm),  $\varepsilon$  = 610 dm<sup>-3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

**Preparation of** [[Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PMe<sub>3</sub>)]<sub>2</sub>] (7-Me). A cold (0 °C) solution of 3-Me (0.60 g, 2.55 mmol) in THF (50 mL) was added to activated Mg (30 mg, 1.23 mmol). The reaction mixture was stirred for 5 h at 0 °C, during which a slow color change from red to green occurred. The resulting green solution was allowed to warm to room temperature, and the volatiles were removed *in vacuo*. The dark green residue was extracted into pentane (10 mL), and the solution was cooled to 9 °C for 48 h, affording 7-Me as dark green needles. Yield: 0.26 g, 53 %. Anal. Calcd for C<sub>16</sub>H<sub>28</sub>Ni<sub>2</sub>P<sub>2</sub>: C, 48.08; H, 7.06; N, 0.00 %. Found: C, 47.89; H, 6.89; N, 0.00 %. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 1.21 (18H, m, CH<sub>3</sub>), 5.38 (10H, s, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) -10.1.

**Preparation of** [**{Ni**( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(P<sup>n</sup>Pr<sub>3</sub>)<sub>2</sub>] (7-<sup>n</sup>Pr). A cold (0 °C) solution of 3-"Pr (1.55 g, 4.86 mmol) in THF (50 mL) was added to activated Mg (59 mg, 2.43 mmol). The reaction mixture was stirred for 5 h at 0 °C, during which a slow color change from red to green occurred. The resulting green solution was allowed to warm to room temperature, and the volatiles were removed *in vacuo*. The dark green residue was extracted into pentane (10 mL), and the solution was cooled to 9 °C for 24 h, affording 7-"Pr as dark green blocks. Yield: 1.10 g, 80 %. Anal. Calcd for C<sub>28</sub>H<sub>52</sub>Ni<sub>2</sub>P<sub>2</sub>: C, 59.20; H, 9.23; N, 0.00 %. Found: C, 59.02; H, 9.51; N, 0.00 %. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 0.97 (18H, m, CH<sub>3</sub>), 1.33 (12H, m, CH<sub>2</sub>), 1.69 (12H, m, PCH<sub>2</sub>) 5.37 (10H, s, C<sub>5</sub>H<sub>5</sub>). Due to poor solubility, no <sup>13</sup>C{<sup>1</sup>H} NMR data could be obtained. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 295 K): δ (ppm) 18.0.

**Preparation of** [{Ni( $\mu$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>P('Bu)<sub>2</sub>)}<sub>2</sub>] (8). A solution of 6 (4.53 g, 13.68 mmol) in THF (30 mL) was added dropwise to cold (-78 °C) activated Mg (0.393 g, 16.17 mmol). The reaction mixture was allowed to warm to 0 °C and stirred at this temperature for 4 h. The solvent was removed *in vacuo* to afford a complex mixture of products as a sticky dark brown/green solid. Recrystallization of a portion from toluene afforded a small crop of dark green crystals of 8 suitable for X-ray crystallographic analysis. Yield < 3%. Insufficient material for full analysis.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00708.

Crystallographic details and data, structure of 7-Me in the solid state, NMR spectra, and DFT computational details (PDF)

Coordinates of optimized structures (XYZ)

## **Accession Codes**

CCDC 1940201–1940212 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

Stephen T. Liddle – Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom;
orcid.org/0000-0001-9911-8778; Email: steve.liddle@manchester.ac.uk

#### Authors

- Peter A. Cleaves Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom
- Alexander J. Ayres School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom
- Lisa Vondung Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom
- John C. Stewart School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom
- Philip J. Cobb Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom
- Ashley J. Wooles Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0001-7411-9627

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00708

#### Notes

The authors declare no competing financial interest.

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