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Synthesis and structures of mononuclear 3,4-bis(trifluoromethyl)pyrrolyl complexes of Rh(i) and Ni(ii)[†]

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New mononuclear complexes of the 3,4-bis(trifluoromethyl)pyrrolyl ligand (3,4-(CF₃)₂-Pyr[−]) with Rh(i) and Ni(ii) are reported. Reaction of 3,4-(CF₃)₂-PyrNa with [Rh(COD)Cl]₂ produces [Rh(PMe₃)₃(3,4-(CF₃)₂-Pyr)] (**1**) while reaction of 3,4-(CF₃)₂-PyrH with [Ni(PMe₃)₂Me₂] (**2**) or [Ni(PMe₃)₂Ph₂] (**4**) gives [*trans*-Ni(PMe₃)₂(3,4-(CF₃)₂-Pyr)(CH₃)] (**3**) or [*trans*-Ni(PMe₃)₂(C₆H₅)(3,4-(CF₃)₂-Pyr)] (**5**) respectively. Complexes **1**, **3** and **5** have been characterized spectroscopically and all five compounds have been structurally characterized by single crystal X-ray diffraction studies.

Introduction

There are many examples where pyrrole based moieties contribute to the overall structures of macrocyclic and porphyrin ligands and a significant number of examples where a deprotonated pyrrole (pyrrolyl, Pyr) acts as a ligand to a transition metal.^{1–5} One example is [Ni(PMe₃)₂(Pyr)Cl] which has been structurally characterized and was investigated for growing metal containing thin films through oxidative polymerization of the pyrrole.^{6,7} There are other reports of nickel pyrrolyl complexes, most of which were prepared over 30 years ago, and characterized spectroscopically using mainly IR and NMR. The earliest report of a nickel-pyrrolyl complex was in 1969 by Jonas and Wilke from the oxidative addition of pyrrole across a zero-valent nickel complex [Ni(P(C₆H₁₁)₃)₃] to give [Ni(P(C₆H₁₁)₃)₂(Pyr)H].⁸ The nickel hydride stretch was found easily in the IR at 1910 cm^{−1} and was the only proof that the complex was successfully synthesized. A year later two more reports came out detailing the synthesis of [Ni(PR₃)₂(NC₄H₄)₂] with various alkyl phosphines and [Ni(PPh₃)₂(Cp)(NC₄H₄)] using potassium pyrrolide and the corresponding nickel dibromide salts or lithium pyrrolide and [Ni(PPh₃)₂(Cp)Cl] respectively.^{9,10} Others have reported nickel nitrosyl complexes synthesized with potassium pyrrolide in the presence triphenylphosphine and NO from nickel bromide.¹¹ More recently, Garcia and others have reported a complex in which the N–H bond of pyrrole was

oxidatively added to a Ni(0) phosphine complex, although it was not structurally characterized.¹²

There appear to be very few examples of non-chelating substituted pyrrolyl complexes. An example for nickel is the report by Carmona and coworkers who studied complexes of both unsubstituted pyrrolyl as well as 3,4-dimethylpyrrolyl ligands in *trans*-bis(trimethylphosphine) complexes with alkyls and aryls.¹³ These complexes were under investigation as potential carbonylation and carboxylation catalysts. As part of a program aimed at the development of new ligands for CVD or ALD precursors we have investigated the synthesis of new complexes of the 3,4-bis(trifluoromethyl)pyrrolyl ligand (3,4-(CF₃)₂-NHC₄H₂ or 3,4-(CF₃)₂-PyrH). This ligand was chosen because it is similar in size and structure to the well-known 3,5-bis trifluoromethyl pyrazolate.¹⁴ It should have increased volatility compared to the unsubstituted pyrrolyl ligand by virtue of the two CF₃ groups and bind in a monodentate fashion leading to the formation of mononuclear complexes (*vs.* higher nuclearity, less volatile species). We report here new mononuclear complexes of 3,4-(CF₃)₂-Pyr with Rh(i) and Ni(ii) and also single crystal X-ray diffraction studies on [*trans*-Ni(PMe₃)₂(CH₃)₂] and [*trans*-Ni(PMe₃)₂(C₆H₅)₂] which, so far, do not appear to have been structurally characterized.

Results and discussion

Synthesis of rhodium pyrrolyl complex [Rh(PMe₃)₃(3,4-(CF₃)₂-Pyr)] (**1**)

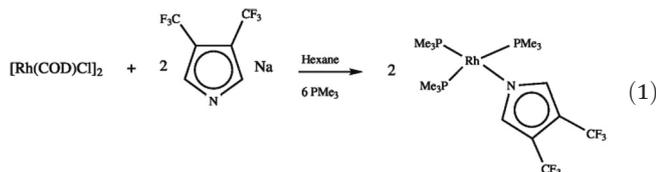
CAUTION: There have been explosions with related alkali metal pyrrolyl CF₃ species.¹⁵ Although we have never experienced an explosion we recommend that alkali metal salts of the pyrrolyl derivative should not be isolated.

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The synthesis of Rh-3,4-(CF₃)₂-Pyr complexes from the lithium salt 3,4-(CF₃)₂-PyrLi was unsuccessful, despite the fact that other groups had found success with this route using unsubstituted pyrroles.⁸ However, the sodium salt, generated by reaction of 3,4-(CF₃)₂-PyrH with NaH, and used *in situ*, was successfully used to synthesize the new complex [Rh(PMe₃)₃(3,4-(CF₃)₂-Pyr)] (**1**) (eqn (1)). Thus, reaction of a mixture of [Rh(COD)Cl]₂ and PMe₃ with two equivalents of 3,4-(CF₃)₂-PyrNa in hexane afforded **1** in high yield (72%). There appear to be few examples of Rh-Pyr complexes where the pyrrolyl moiety is not part of a macrocyclic entity or functionalized with a chelating group.



Eqn (1) Synthetic route to rhodium pyrrolyl complex.

There are a few known Rh-Pyr complexes which incorporate CO and PR₃ groups and these include those with a monodentate pyrrolyl ligand of the type [Rh(PR₃)(CO)(Pyr)] such as [*trans*-Rh(PPh₃)₂(CO)(2,5-Me₂-Pyr)] and [*trans*-Rh(PMe₃)₂(CO)-(2,5-((CH₃)₂-furyl)₂-3,4-(COCH₃)₂-Pyr)].^{16,17} There are numerous examples of Rh(I) complexes of the type [Rh(PMe₃)₃X] including the previously described pyrazolate complex [Rh(PMe₃)₃-(3,5-(CF₃)₂-Pz)]¹⁸ but **1** appears to be the first reported pyrrolyl compound with this general formula.

Complex **1** crystallizes in the orthorhombic space group *Pnma* with the metal coordination plane lying on a crystallographic mirror plane resulting in one half of a molecule in the asymmetric unit and four independent molecules in the unit cell. Fig. 1 shows the overall molecular geometry and atom numbering scheme with crystallographic details given in Table 1 and a listing of key bond lengths and angles in Table 2. The geometry around the Rh(I) center is square planar

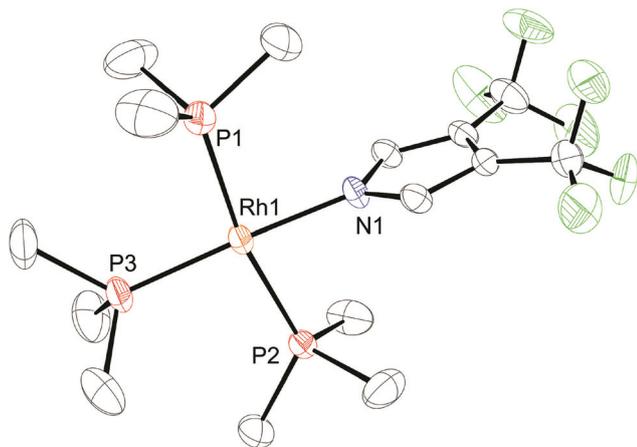


Fig. 1 ORTEP view of **1** with partial atom numbering scheme. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

with some distortion towards tetrahedral likely due to steric crowding. The pair of *trans* PMe₃ ligands are bound so that there is a slight deviation in the P–Rh–P angle from 180° (P(1)–Rh–P(2) 177.49(13)°, with the N(1)–Rh–P(3) angle more distorted (169.27(5)°). As found in the analogous 3,5-(CF₃)₂-Pz complex, the Rh–P bond *trans* to the pyrrolyl is shorter (2.2268(15) Å) than the mutually *trans* Rh–P bonds (avg. 2.3118(16) Å) by 0.0845(12) Å.¹² The plane of the pyrrolyl ligand is oriented perpendicular to the Rh coordination plane, and this minimizes steric interactions between the PMe₃ and CF₃ groups. This was also observed in [Rh(PMe₃)₃(3,5-(CF₃)₂-Pz)].¹⁸

The ³¹P NMR spectrum of **1** contains a well resolved doublet of triplets centered at –3.12 ppm (*J*_{P–Rh} = 149.5 Hz, *J*_{P–P} = 45.8 Hz) assigned to P *trans* to 3,4-(CF₃)₂-Pyr. There is also a doublet of doublets centered at –12.06 ppm (*J*_{P–Rh} = 134.1 Hz, *J*_{P–P} = 45.2 Hz). The ¹⁹F NMR spectrum contains a singlet at –54.2 ppm assigned to the two equivalent CF₃ groups. The complex was tested for volatility in a sealed tube under vacuum (0.1 torr) and found to sublime without melting at 108 °C to give X-ray quality crystals that confirmed it was unchanged after sublimation.

Synthesis of nickel pyrrolyl complexes

Several groups, including those of Schrock and Hoveyda, have successfully utilized unsubstituted lithium pyrrolide as a metalation reactant.¹⁹ However, in our hands attempts to prepare 3,4-(CF₃)₂-Pyr complexes of Ni *via* salt elimination routes using 3,4-(CF₃)₂-PyrLi or 3,4-(CF₃)₂-PyrNa were unsuccessful. Reaction of *n*-BuLi with 3,4-(CF₃)₂-PyrH in THF or diethyl ether at –78 °C resulted in black solutions after only a few minutes. Starting materials were recovered in high yields from reactions of these solutions with a variety of Ni(II) based compounds. In previous work by the Hartwig group and others unsubstituted sodium pyrrolide was generated with NaH.⁵ This was used for NaCl eliminations with metal chlorides, but similar attempts using 3,4-(CF₃)₂-PyrNa were unsuccessful and starting materials were again recovered. Parkin has demonstrated that pyrrole could be substituted onto titanium complexes *via* an alkane elimination route using Ti-alkyl complexes,²⁰ and since nickel alkyl and aryl complexes are well-known this route was explored successfully. Thus the reaction of excess 3,4-(CF₃)₂-PyrH with [*trans*-Ni(PMe₃)₂(CH₃)₂] or [*trans*-Ni(PMe₃)₂(C₆H₅)₂] resulted in substitution of only one of the alkyl or aryl groups (Scheme 1). Both [*trans*-Ni(PMe₃)₂(CH₃)₂] and [*trans*-Ni(PMe₃)₂(C₆H₅)₂] do not appear to have been structurally characterized previously. The structures were therefore determined by single crystal X-ray crystallography and they provided valuable structural information for comparative purposes, as well as unequivocally establishing the structures of the compounds.

[*trans*-Ni(PMe₃)₂(CH₃)₂] (**2**). Although *trans*-dimethyl-bis(trimethylphosphine)nickel(II) was first synthesized and characterized almost 40 years ago by Klein and Karsh, there has never been an investigation of the solid state structure by single crystal X-ray diffraction.²¹ This is likely due to the extreme air-sensitive, thermal instability, and potentially pyrophoric nature of **2**. The complex was prepared by a slightly modified

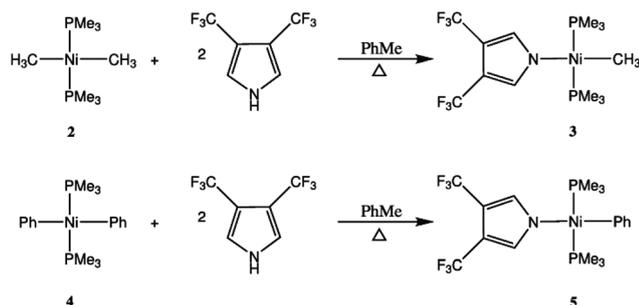
Table 1 Crystallographic data for compounds 1–5

	1	2	3	4	5
Empirical formula	C ₁₅ H ₂₉ F ₆ NP ₃ Rh	C ₈ H ₂₄ P ₂ Ni	C ₁₃ H ₂₃ F ₆ NP ₂ Ni	C ₁₈ H ₂₈ P ₂ Ni	C ₁₈ H ₂₅ F ₆ NP ₂ Ni
Formula weight	533.21	240.92	427.97	365.05	490.04
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	<i>Pnma</i>	<i>P21/c</i>	<i>P21/c</i>	<i>P1</i>	<i>P21/n</i>
Unit cell dimensions					
<i>a</i> (Å)	15.096(2)	5.410(5)	9.4460(13)	6.3114(7)	14.992(5)
<i>b</i> (Å)	11.8371(19)	15.773(3)	19.127(3)	8.6172(10)	8.881(3)
<i>c</i> (Å)	13.136(2)	8.449(5)	11.7898(16)	18.474(2)	17.857(6)
α (°)	90	90	90	82.806(4)	90
β (°)	90	118.57(4)	116.467(3)	89.043(5)	110.989(5)
γ (°)	90	90	90	68.545(4)	90
<i>V</i> (Å ³)	2347.3(6)	633.2(7)	1906.9(5)	927.29(18)	2219.8(13)
<i>Z</i>	4	2	4	2	4
<i>D</i> _{calc} (g cm ⁻³)	1.509	1.264	1.491	1.307	1.466
μ (mm ⁻¹)	0.978	1.736	1.234	1.211	1.071
<i>F</i> (000)	1080	260	880	388	1008
θ range (°)	3.10–27.48	2.58–25.00	3.15–27.48	3.17–26.50	1.53–27.50
Reflections collected	32 094	3741	14 114	7798	9292
Unique reflections	2815	1099	4366	3755	5006
<i>R</i> _{int}	0.0634	0.0789	0.0548	0.0310	0.0464
Reflns used	2815	1099	4366	3755	5006
Restraints	102	148	0	0	0
Params	162	99	215	199	259
Goodness-of-fit	1.044	1.257	1.033	1.093	0.984
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0431 <i>wR</i> ₂ = 0.0958	<i>R</i> ₁ = 0.1035 <i>wR</i> ₂ = 0.1846	<i>R</i> ₁ = 0.0406 <i>wR</i> ₂ = 0.0842	<i>R</i> ₁ = 0.0288 <i>wR</i> ₂ = 0.0777	<i>R</i> ₁ = 0.0686 <i>wR</i> ₂ = 0.1553
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0711 <i>wR</i> ₂ = 0.1071	<i>R</i> ₁ = 0.1275 <i>wR</i> ₂ = 0.1965	<i>R</i> ₁ = 0.0579 <i>wR</i> ₂ = 0.0907	<i>R</i> ₁ = 0.0320 <i>wR</i> ₂ = 0.0798	<i>R</i> ₁ = 0.0956 <i>wR</i> ₂ = 0.1766
Absolute structure parameter					
Largest difference between peak and hole (e Å ⁻³)	0.381 and −0.713	1.083 and −0.704	0.547 and −0.419	0.430 and −0.417	0.689 and −0.475

$$^a R_1 = \sum_{hkl} (|F_o| - |F_c|) / \sum_{hkl} |F_o|, R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Table 2 Selected bond lengths (Å) and angles (°) for 1

Bond lengths		Bond angles	
Rh(1)–N(1)	2.087(4)	P(1)–Rh(1)–P(2)	169.27(5)
Rh(1)–P(3)	2.2268(15)	N(1)–Rh(1)–P(3)	177.49(13)
Rh(1)–P(1)	2.2972(17)	N(1)–Rh(1)–P(1)	86.22(13)
Rh(1)–P(2)	2.3263(15)	P(3)–Rh(1)–P(1)	96.29(6)
		N(1)–Rh(1)–P(2)	83.05(13)



Scheme 1 Synthetic route to nickel pyrrolyl complexes.

procedure as described previously. Methyl lithium was added dropwise to a diethyl ether solution of [Ni(PMe₃)₂Cl₂] at −78 °C. This was warmed to −5 °C and stirred for 2 hours. After volatiles were removed *in vacuo*, extraction of the residue

with cold hexane (−5 °C) and cooling to −30 °C afforded yellow needles of 2. The reaction was not allowed to warm above −5 °C since the product was found to be thermally unstable.

Complex 2 crystallizes in the monoclinic space group *P2₁/c* with the unique Ni atom sitting on an inversion center. This results in only half of the molecule in the asymmetric unit with one unique PMe₃ group and one Ni bound methyl (Fig. 2). Crystallographic details are given in Table 1 and selected bond lengths and angles are given in Table 3. The Ni center has a square planar coordination geometry with a C(1)–Ni(1)–P(1) bond angle of 88.5(9)° and bond lengths of 2.145(3) Å and 1.987(5) Å for Ni–P and Ni–C respectively. When compared to the starting material [Ni(PMe₃)₂Cl₂], the Ni–P bond lengths are slightly shorter for 2 by 0.08(2) Å. All other spectroscopic data were in accord with previously published values.¹⁷

[*trans*-Ni(PMe₃)₂(3,4-(CF₃)₂-Pyr)(CH₃)] (3). The treatment of 2 with two equivalents of 3,4-(CF₃)₂-PyrH at −10 °C in toluene followed by a slow warming, heating to reflux and reaction time of 8 hours resulted in a yellow solution of 3. Removal of the volatiles *in vacuo* and crystallization from hexane at −30 °C afforded bright yellow prisms of 3 in 74% yield which were suitable for X-ray diffraction studies. The reaction proceeds slowly at room temperature and after several hours a mixture of 2 and 3 is produced. Interestingly only one Ni–Me group is replaced even after prolonged heating of the reaction mixture.

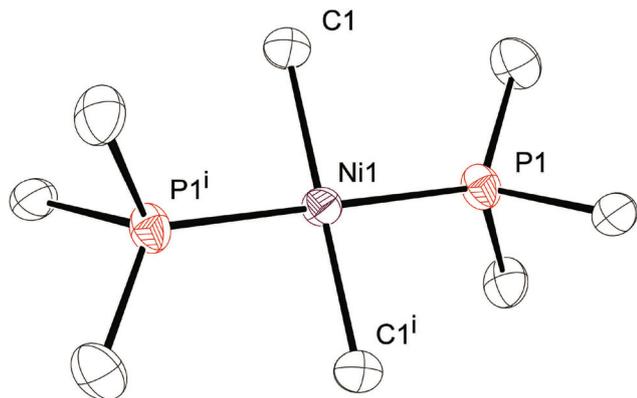


Fig. 2 ORTEP view of **2** with partial atom numbering scheme. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Bond lengths		Bond angles	
Ni(1)–C(1)	1.987(15)	C(1)–Ni(1)–P(1)	88.5(9)
Ni(1)–P(1)	2.145(3)	C(1)–Ni(1)–P(1) ⁱ	91.5(9)
		C(1) ⁱ –Ni(1)–C(1)	180.0(11)
		P(1) ⁱ –Ni(1)–P(1)	180.00(18)

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with four independent molecules in the unit cell. The structure is shown in Fig. 3 with crystallographic details given in Table 1 and selected bond lengths and angles in Table 4. As found for $[\text{Ni}(\text{PMe}_3)_2\text{Cl}_2]$, the geometry of the Ni center is pseudo-square planar. The structure is slightly distorted towards tetrahedral with P(1)–Ni(1)–P(2) and C(1)–Ni(1)–N(1) bond angles of $174.52(3)^\circ$ and $173.66(11)^\circ$ respectively. The Ni–PMe₃ lengths are similar for Ni–P(1) and Ni–P(2) at 2.1830(7) Å and 2.2002(7) Å respectively. There is only a slight lengthening of these bonds from that found in **2**, which has a Ni–P bond length of 2.145(3) Å. There is a reduction in the Ni–Me bond length compared to the starting material (1.987(15) Å and 1.943(3) Å) for **2** and **3** respectively. Although this is relatively small, this may be an indication of the *trans*-influence of the pyrrolyl ligand. Since there is only one other structurally characterized nickel pyrrolyl complex to compare with, [*trans*-Ni(PMe₃)₂Cl(Pyr)], it is difficult to provide an in-depth comparative discussion on the nature of the nickel–pyrrolyl bonding. The Ni–N bond length in the chloride complex is slightly shorter than that found in **3** (1.883(3) vs. 1.942(2) Å). This is possibly due to the difference in the *trans* ligand, CH₃ vs. Cl, or the presence of the electron-withdrawing CF₃ groups. Both complexes contain the pyrrolyl ring oriented perpendicular to the Ni coordination plane. This is no doubt due to steric restraints, as in both cases, a parallel orientation would be met with severe crowding between the α -carbons and hydrogens of the pyrrolyl and the PMe₃ ligands.

NMR spectroscopic data for **3** in C₆D₆ is consistent with the solid state structure. The ¹H NMR spectrum contains a methyl

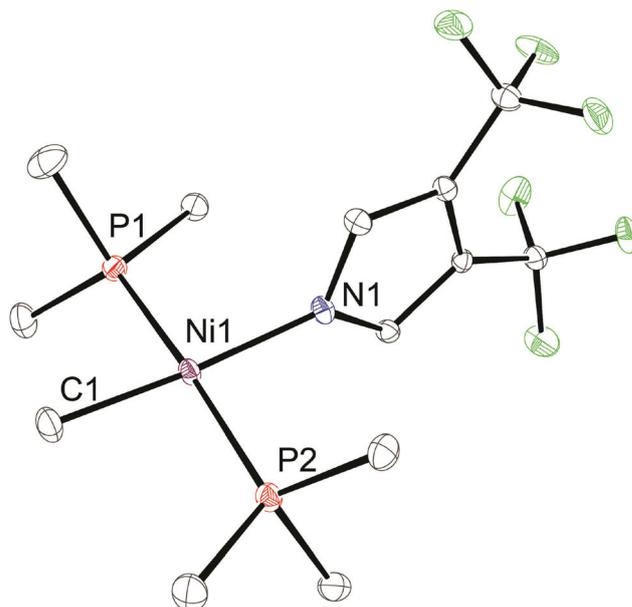


Fig. 3 ORTEP view of **3** with partial atom numbering scheme. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) for **3**

Bond lengths		Bond angles	
Ni(1)–N(1)	1.942(2)	N(1)–Ni(1)–P(1)	91.62(6)
Ni(1)–C(1)	1.943(3)	C(1)–Ni(1)–P(1)	88.18(8)
Ni(1)–P(1)	2.1830(7)	N(1)–Ni(1)–P(2)	90.09(6)
Ni(1)–P(2)	2.2002(7)	C(1)–Ni(1)–P(2)	90.68(8)
		N(1)–Ni(1)–C(1)	173.66(11)
		P(1)–Ni(1)–P(2)	174.52(3)

resonance at -0.96 ppm which is consistent with other Ni–Me complexes. The PMe₃ protons are observed as a singlet at 0.42 ppm and the aryl protons are a singlet at 6.94 ppm. Integration of the peaks is consistent with a 3 : 18 : 2 ratio. The ¹⁹F and ³¹P NMR spectra both consist of sharp single peaks at -54.71 and -11.01 ppm respectively. The volatility of the complex was investigated in a similar manner as before and it sublimes without melting in the range 125–130 °C. After the sublimation was complete, the isolation of single crystals and an X-ray diffraction study confirmed to **3** to be stable under the conditions of the sublimation process.

[*trans*-Ni(PMe₃)₂(C₆H₅)₂] (**4**). The diphenyl nickel complex, *trans*-diphenyl-bis(trimethylphosphine)nickel(II) was described in 2005, although there appears to be no recorded structural study in the literature.²² The complex is moderately air stable, with noticeable decomposition occurring over the course of 24 hours. In contrast to the original report, in our hands, it is thermally stable at room temperature though not at temperatures higher than 35 °C.

The complex was prepared by a slightly modified procedure as described previously.²² Phenyllithium was added dropwise

to a diethyl ether solution of $[\text{Ni}(\text{PMe}_3)_2\text{Cl}_2]$ at $-78\text{ }^\circ\text{C}$. This was warmed to room temperature and stirred for 4 hours. The volatiles were removed *in vacuo*. Extraction of the residue with hexane and cooling to $-30\text{ }^\circ\text{C}$ afforded yellow plates of **4** suitable for study by X-ray diffraction.

Complex **4** crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically unique Ni centers in the asymmetric unit, both of which lie on crystallographic inversion centers. Two half molecules are in the asymmetric unit with two independent molecules in the unit cell. The structure is shown in Fig. 4 with crystallographic details given in Table 1 and selected bond lengths and angles given in Table 5. There is virtually no distortion of the square planar geometry towards tetrahedral with P–Ni–P bond angles of 180° and average P–Ni–C angles of $90.61(6)^\circ$. The Ni–P bonds are slightly longer than those found in the Me analogue **2** ($2.1650(4)\text{ \AA}$ vs. $2.145(3)\text{ \AA}$). This is likely a result of the greater electron withdrawing ability of the phenyl rings *versus* the methyl groups resulting in less Ni–P π -bonding with the phosphines. The average Ni–C(Ph) bond length is $1.9372(17)\text{ \AA}$. NMR and IR spectroscopic data were consistent with previously published values.²²

[trans-Ni(PMe₃)₂(C₆H₅)₂(3,4-(CF₃)₂-Pyr)] (**5**). The treatment of **4** with two equivalents of 3,4-(CF₃)₂-PyrH at room temperature

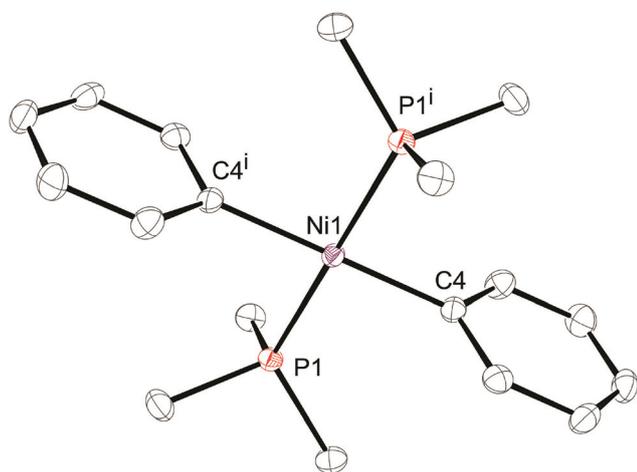


Fig. 4 ORTEP view of one of the independent molecules of **4** with partial atom numbering scheme. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for both molecules of **4**

Bond angles		Bond lengths	
Ni(1)–P(1)	2.1639(5)	C(4)–Ni(1)–P(1)	90.70(5)
Ni(2)–P(2)	2.1660(5)	C(4)–Ni(1)–P(1) ⁱ	89.30(5)
Ni(1)–C(4)	1.9377(18)	C(13)–Ni(2)–P(2)	90.52(5)
Ni(2)–C(13)	1.9366(18)	C(13)–Ni(2)–P(2) ⁱ	89.48(5)
		P(1)–Ni(1)–P(1)	180.000(18)
		C(4)–Ni(1)–C(4) ⁱ	180.000(1)
		P(2)–Ni(2)–P(2) ⁱ	180.00(3)
		C(13) ⁱ –Ni(2)–C(13)	180.00(13)

in toluene followed by heating to reflux and reaction time of 12 hours resulted in a yellow solution of **5**. Removal of the volatiles *in vacuo* and crystallization of the residue from hexane at $-30\text{ }^\circ\text{C}$ afforded bright yellow prisms of **5** in 78% yield which were suitable for X-ray diffraction analysis. The reaction proceeds slowly at room temperature giving a mixture of **4** and **5** after several hours.

Complex **5** crystallizes in the monoclinic space group $P2_1/n$ with four independent molecules per unit cell. The structure of one molecule is shown in Fig. 5 with crystallographic details given in Table 1 and selected bond lengths and angles given in Table 6. The overall geometry features a slightly distorted square planar Ni center, though there is some distortion towards a square pyramidal geometry. The N(1)–Ni(1)–C(1) bond angle is $175.0(2)^\circ$ and P(1)–Ni(1)–P(2) is $175.34(5)^\circ$. Both are distorted towards the same side of the Ni coordination plane. This is possibly a result of packing forces as this distortion forces all of the ligands away from a nearby CF₃ group from an adjacent molecule. The Ni–P bond lengths are slightly longer than those found for the starting material, $[\text{Ni}(\text{PMe}_3)_2\text{Ph}_2]$ **4** ($2.1917(9)\text{ \AA}$ and $2.1650(4)\text{ \AA}$ in **5** and **4** respectively). A similar pattern to that observed in the Ni–Me complexes is also observed for the Ni–Ph complexes with a reduction of the Ni–C(Ph) bond length from $1.9372(17)\text{ \AA}$ to $1.908(4)\text{ \AA}$ in **4** and **5** respectively. This effect is observed in the chemical shifts of the phenyl protons in the ¹H NMR in C₆D₆ where all of the resonances are shifted upfield to 6.79, 6.91, and 6.95 ppm from the diphenyl precursor where they are observed at 7.02, 7.19, and 7.60 ppm for the *para*-, *meta*-, and *ortho*-protons respectively. A classic pseudo-triplet at

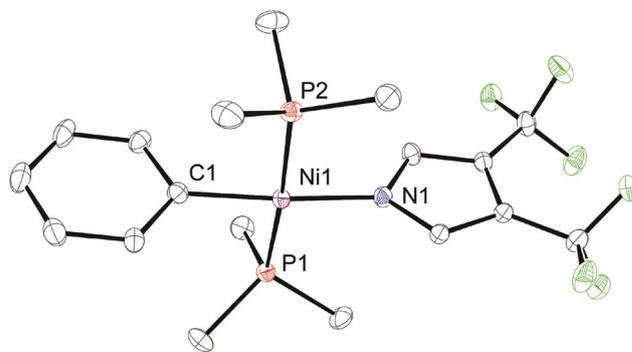


Fig. 5 ORTEP view of **5** with partial atom numbering scheme. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for **5**

Bond angles		Bond lengths	
Ni(1)–C(1)	1.908(4)	C(1)–Ni(1)–P(1)	89.43(14)
Ni(1)–N(1)	1.924(4)	N(1)–Ni(1)–P(1)	91.48(12)
Ni(1)–P(1)	2.1879(14)	C(1)–Ni(1)–P(2)	87.39(14)
Ni(1)–P(2)	2.1954(13)	N(1)–Ni(1)–P(2)	91.40(12)
		C(1)–Ni(1)–N(1)	174.98(18)
		P(1)–Ni(1)–P(2)	175.34(5)

0.241 ppm ($|^2J_{P,H} + ^4J_{P,H}| = 3.6$ Hz) is observed for the mutually *trans* PMe₃ ligands. The ¹⁹F and ³¹P NMR spectra consist of singlets at -54.71 and -12.71 ppm respectively. The ¹⁹F shift is almost identical for the phenyl and the methyl substituted nickel complexes. The ³¹P resonance is shifted downfield by 1.7 ppm from the methyl analogue **3**.

Compound **5** is volatile 30 °C below the melting point at 138–140 °C. Slow sublimation of the complex (0.1 torr) allowed growth of crystals suitable for an X-ray diffraction study which revealed that the compound is unchanged after sublimation. When the complex was sublimed by heating rapidly at 0.1 torr it began to decompose at 175 °C.

Conclusions

We report the synthesis and structures of new complexes of the substituted pyrrolyl 3,4-(CF₃)₂-Pyr with Rh(i) and Ni(ii) based PMe₃ complexes. The compounds are sufficiently volatile to serve as precursors for CVD and these studies are in progress.

Experimental

General procedures

CAUTION: There have been explosions with related alkali metal pyrrolyl CF₃ species.¹⁵ Although we have never experienced an explosion we recommend that alkali metal salts of the pyrrolyl derivative should not be isolated.

All reactions were performed under a dry, oxygen-free nitrogen atmosphere or under vacuum using standard Schlenk line and dry box techniques. Solvents were dried prior to use by distillation from sodium benzophenone ketyl anion under nitrogen. The compounds 3,4-bis(trifluoromethyl)pyrrole (3,4-(CF₃)₂-PyrH),²³ [Rh(COD)Cl]₂,²⁴ [Ni(PMe₃)₂Cl]₂,²⁵ [Ni(PMe₃)₂-Me₂],²¹ and [Ni(PMe₃)₂(C₆H₅)₂]²² were prepared as previously described. Trimethylphosphine (97%) and *n*-butyl lithium (1.6 M in hexane) were purchased from Aldrich and used without further purification.

Instrumental details

NMR spectra were recorded on a Varian 300 Unity spectrometer (¹H, 300 MHz; ¹⁹F, 282 MHz; ³¹P, 121 MHz) at 25 °C. ¹H NMR signals are reported relative to residual proton resonances in deuterated solvents. Electrospray Ionization (ESI) mass spectra were recorded on a Thermo-Fisher LTQ. Infrared spectra were recorded using a Nicolet IR 200 FTIR spectrometer using attenuated total reflectance (ATR). Microanalysis (C, H, N) were performed by Galbraith Laboratories of Knoxville, TN or QTI Labs of Whitehouse, NJ. Melting points were obtained using an Electrothermal resistively heated melting point apparatus in sealed glass capillaries under a dinitrogen atmosphere or 0.1 torr vacuum.

X-Ray Experimental: all crystals were mounted on a glass fiber. The data was collected on either a Nonius Kappa CCD

diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073$ Å) at reduced temperature using an Oxford Cryostream low temperature device or a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoK α radiation at reduced temperature using a Rigaku XStream low temperature device. Data reduction was performed with either DENZO-SMN²⁶ or Rigaku America's Corporation's Crystal Clear version 1.40. The structures were solved by direct methods using SIR97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.²⁷ The absolute configuration was assigned by internal comparison to the known absolute configuration of selected portions of the molecule. The hydrogen atoms on carbon were calculated in idealized positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom ($1.5 \times U_{eq}$ for methyl hydrogen atoms). The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0528P)^2 + (0.685P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).²⁸ All figures were generated using SHELXTL/PC.

[Rh(PMe₃)₃(3,4-(CF₃)₂-Pyr)] (1). A solution of 3,4-(CF₃)₂-PyrH (0.42 g, 2.07 mmol) in hexane (50 ml) was added to a suspension of NaH (0.059 g, 2.48 mmol) in hexane (50 ml) at room temp. and stirred for 4 hours. In a separate flask PMe₃ (0.46 g, 6.18 mmol) was added dropwise to a suspension of [Rh(COD)-Cl]₂ (0.51 g, 1.03 mmol) in hexane (80 ml) and added to the suspension of 3,4-(CF₃)₂-PyrNa. Stirring for 8 hours resulted in a color change of the suspension from orange to yellow. The reaction was filtered and the filtrate evaporated to dryness. Extraction of the residue with hexane (2 × 150 ml) and cooling (-25 °C) gave yellow prisms of **1**. Isolated yield: 0.79 g, 72%. m.p. 121–123 °C. (1 atm N₂); 108–110 °C sublimes (0.1 torr). ¹H NMR (300 MHz, C₆D₆, 27 °C) δ 7.17 (s, 2H, Ar-H), 0.64 (d, $J_{H-P} = 7.4$ Hz, 9H, P-CH₃), 0.67 (t, $|^2J_{P-H} + ^4J_{P-H}| = 2.6$ Hz, 18H, P-CH₃). ¹⁹F NMR (282 MHz, C₆D₆) δ -54.20 (s, CF₃). ³¹P{¹H} NMR (121 MHz, C₆D₆) δ -3.12 (dt, $J_{P-Rh} = 149.5$ Hz, $J_{P-P} = 45.8$ Hz, 1P), -12.06 (dd, $J_{P-Rh} = 134.1$ Hz, $J_{P-P} = 45.2$ Hz, 2P). MS m/z 331 [M⁺, -Pyr]; 255 [M⁺, -Pyr, -PMe₃]. FT-IR (ATR, cm⁻¹): 2916 (w), 1656 (w), 1527 (w), 1418 (w), 1350 (w), 1299 (m), 1255 (m), 1216 (w), 1142 (s), 1118 (vs), 1021 (w), 1003 (w), 943 (v), 867 (m), 853 (m), 810 (m), 750 (m). Anal. Found: C, 29.1; H, 5.0; N, 4.8. Calc.: C, 28.3, H, 4.6; N, 5.1%.

***trans*-Ni(PMe₃)₂(3,4-(CF₃)₂-Pyr)(CH₃) (3).** A solution of 3,4-(CF₃)₂-PyrH (0.120 g, 0.591 mmol) in toluene (30 ml) was added to solution of [*trans*-Ni(PMe₃)₂(CH₃)₂] (0.072 g, 0.296 mmol) in toluene (80 ml). The mixture was stirred and refluxed for 8 hours. The volatiles were removed *in vacuo* and the residue extracted with hexane (120 ml) and filtered. The volume of the filtrate was reduced (40 ml) and cooling (-30 °C) gave yellow plates of **3**. Isolated yield: 0.094 g, 74%. m.p. 134–137 (1 atm N₂) 125–130 sublimes (0.1 torr). ¹H NMR (300 MHz, C₆D₆): δ -0.96 (s, 3 H, Ni-CH₃), 0.42 (s, 18H, P-CH₃), 6.94 (s, 2H, Pyrrole-H); ¹⁹F NMR: (282 MHz, C₆D₆): δ -54.71 (s, CF₃); ³¹P NMR: (121 MHz, C₆D₆): δ -11.01 (s). FTIR (ATR, cm⁻¹): 2909

vw, 1543 m, 1506 w, 1427 w, 1051 m, 1326 m, 1288 w, 1260 w, 1142 s, 1098 vs, 976 m, 943 vs, 853 w, 831 m, 735 m. EI/MS m/z : 225 [M^+ , -Pyr] 167 [M^{2+} , -PMe₃, -CH₃, -H]. Anal. Found: C, 36.0, H, 5.0; N, 3.1. Calc.: C, 36.5; H, 5.4; N, 3.3%.

trans-Ni(PMe₃)₂(3,4-(CF₃)₂-Pyr)(C₆H₅) (5). A solution of 3,4-(CF₃)₂-PyrH (0.180 g, 0.886 mmol) in toluene (30 ml) was added to solution of [trans-Ni(PMe₃)₂(C₆H₅)₂] (0.15 g, 0.443 mmol) in toluene (80 ml). The mixture was stirred and refluxed for 12 hours. The volatiles were removed *in vacuo* and the residue extracted with hexane (120 ml) and filtered. The volume of the filtrate was reduced (50 ml) and cooling (-30 °C) gave yellow plates of 5. Isolated yield: 0.17 g, 78%. m. p. 163–166 (1 atm N₂) 138–140 sublimes (0.1 torr). ¹H NMR (300 MHz, C₆D₆) δ 0.241 (t, 18 H, P-CH₃, (²J_{P,H} + ⁴J_{P,H}) = 3.6 Hz), 6.79 (t, 1H, H-*p*), 6.91 (m, 2H, H-*m*) 6.95 (s, 2H, Pyr-H), 7.08 (m, 2H, H-*o*); ¹⁹F NMR: (282 MHz, C₆D₆): δ -54.71 (s, 6 F, -CF₃); ³¹P NMR: (121 MHz, C₆D₆): δ -12.71 (s, 2P). FTIR (ATR, cm⁻¹) 3048 vw, 2978 vw, 2909 vw, 1546 m, 1510 w, 1454 vw, 1421 w, 1361 m, 1327 m, 1281 m, 1261 s, 1236 s, 1147 vs, 1097 vs, 1056 w, 1020 m, 978 s, 945 s, 859 w, 834 w, 799 w, 734 s, 707 m. EI/MS m/z : 287 [M^+ , -Pyr] Anal. Found: C, 43.9; H, 5.1; N, 2.8. Calc.: C, 44.1; H, 5.1; N, 2.9%.

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Notes and references

- Ti, Zr, Hf pyrrolyl complexes: (a) H. Lee, J. B. Bonanno, T. Hascall, J. Cordaro, J. M. Hahn and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1999, 1365; (b) K. Nomura, S. Pracha, K. Phomphrai, S. Katao, D.-H. Kim, H. J. Kim and N. Suzuki, *J. Mol. Catal. A: Chem.*, 2012, **365**, 136; (c) I. Saeed, S. Katao and K. Nomura, *Organometallics*, 2009, **28**, 111; (d) A. Spannenberg, V. V. Burlakov, P. Arndt, M. Klahn and U. Rosenthal, *Z. Kristallogr. – New Cryst. Struct.*, 2007, **222**, 192; (e) K. Black, A. C. Jones, J. Bacsá, P. R. Chalker, P. A. Marshall, H. O. Davies, P. N. Heys, P. O'Brien, M. Afzaal, J. Raftery and G. W. Critchlow, *Chem. Vap. Deposition*, 2010, **16**, 93; (f) J. L. Atwood, R. D. Rogers and R. V. Bynum, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 1812; (g) R. D. Rogers, R. V. Bynum and J. L. Atwood, *J. Crystallogr. Spectrosc. Res.*, 1984, **14**, 21; (h) K.-C. Hsieh, W.-Y. Lee, L.-F. Hsueh, H.-M. Lee and J.-H. Huang, *Eur. J. Inorg. Chem.*, 2006, 2306.
- Cr, Mo, W pyrrolyl complexes: (a) A. G. Lichtscheidl, V. W. L. Ng, P. Muller, M. K. Takase, R. R. Schrock, S. J. Malcolmson, S. J. Meek, B. Li, E. T. Kiesewetter and A. H. Hoveyda, *Organometallics*, 2012, **31**, 4558; (b) N. A. Obaidi, K. P. Brown, A. J. Edwards, S. A. Hollins, C. J. Jones, J. A. McCleverty and B. D. Neaves, *J. Chem. Soc., Chem. Commun.*, 1984, 690; (c) N. A. Obaidi, A. J. Edwards, C. J. Jones, J. A. McCleverty, B. D. Neaves, F. E. Mabbs and D. Collison, *J. Chem. Soc., Dalton Trans.*, 1989, 127; (d) A. J. Jiang, R. R. Schrock and P. Muller, *Organometallics*, 2008, **27**, 4428; (e) R. R. Schrock, A. J. Jiang, S. C. Marinescu, J. H. Simpson and P. Muller, *Organometallics*, 2010, **29**, 5241; (f) S. C. Marinescu, R. Singh, A. S. Hock, K. M. Wampler, R. R. Schrock and P. Muller, *Organometallics*, 2008, **27**, 6570; (g) K. M. Wampler, R. R. Schrock and A. S. Hock, *Organometallics*, 2007, **26**, 6674; (h) H. Jeong, D. J. Kozera, R. R. Schrock, S. J. Smith, J. Zhang, N. Ren and M. A. Hillmyer, *Organometallics*, 2013, **32**, 4843; (i) M. R. Reithofer, G. E. Dobereiner, R. R. Schrock and P. Muller, *Organometallics*, 2013, **32**, 2489; (j) G. Huttner and O. S. Mills, *Chem. Ber.*, 1972, **105**, 301; (k) M. M. Flook, A. J. Jiang, R. R. Schrock, P. Muller and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 7962; (l) J. Yuan, E. M. Townsend, R. R. Schrock, A. S. Goldman, P. Muller and M. K. Takase, *Adv. Synth. Catal.*, 2011, **353**, 1985; (m) S. C. Marinescu, R. R. Schrock, P. Muller, M. K. Takase and A. H. Hoveyda, *Organometallics*, 2011, **30**, 1780; (n) T. Kreickmann, S. Arndt, R. R. Schrock and P. Muller, *Organometallics*, 2007, **26**, 5702; (o) H. Jeong, J. C. Axtell, B. Torok, R. R. Schrock and P. Muller, *Organometallics*, 2012, **31**, 6522.
- Re pyrrolyl complexes: (a) T. J. Johnson, L. J. Alvey, M. Brady, C. L. Mayne, A. M. Arif and J. A. Gladysz, *Chem. – Eur. J.*, 1995, **1**, 294; (b) M. R. DuBois, L. D. Vasquez, L. Peslherbe and B. C. Noll, *Organometallics*, 1999, **18**, 2230.
- Fe, Ru pyrrolyl complexes: (a) T. Morikita, M. Hirano, A. Sasaki and S. Komiya, *Inorg. Chim. Acta*, 1999, **291**, 341; (b) M. Powell, R. D. Bailey, C. T. Eagle, G. L. Schimek, T. W. Hanks and W. T. Pennington, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1611; (c) M. Hirano, K. Onuki, Y. Kimura and S. Komiya, *Inorg. Chim. Acta*, 2003, **352**, 160; (d) K. A. Pittard, T. R. Cundari, T. B. Gunnoe, C. S. Day and J. L. Petersen, *Organometallics*, 2005, **24**, 5015; (e) D. Coucouvanis, A. Salifoglou, M. G. Kanatzidis, A. Simopoulos and V. Papaefthymiou, *J. Am. Chem. Soc.*, 1984, **106**, 6081.
- Re pyrrolyl complex: M. S. Driver and J. F. Hartwig, *Organometallics*, 1998, **17**, 1134.
- T. W. Hanks, M. Mathis and W. Harsha, *Synth. Met.*, 1999, **102**, 1792.
- M. Mathis, W. Harsha, T. W. Hanks, R. D. Bailey, G. L. Schimek and W. T. Pennington, *Chem. Mater.*, 1998, **10**, 3568.
- K. Jonas and G. Wilke, *Angew. Chem., Int. Ed.*, 1969, **8**, 519.
- E. Wenschuh and G. Z. Mahner, *Angew. Chem., Int. Ed. Engl.*, 1970, **10**, 73.
- D. Z. Tille, *Z. Naturforsch., B: Anorg. Chem. Org. Chem. Biochem. Biophys. Biol.*, 1970, **25**, 1358.

- 11 W. Seidel and D. Z. Geinitz, *Angew. Chem., Int. Ed. Engl.*, 1979, **19**, 413.
- 12 C. López, G. Barón, A. Arévalo, M. A. Muñoz-Hernández and J. J. García, *J. Organomet. Chem.*, 2002, **664**, 170.
- 13 E. Carmona, J. M. Marin, P. Palma, M. Paneque and M. L. Poveda, *Inorg. Chem.*, 1989, **28**, 1895.
- 14 (a) W. J. McCarty, X.-P. Yang, L. J. D. Anderson and R. A. Jones, *Dalton Trans.*, 2012, **41**, 173; (b) J. H. Rivers and R. A. Jones, *Dalton Trans.*, 2013, **42**, 12898.
- 15 D. I. Swartz II and A. L. Odom, *Organometallics*, 2007, **26**, 6684.
- 16 K. Yünlü, F. Basolo and A. L. Rheingold, *J. Organomet. Chem.*, 1987, **330**, 221.
- 17 E. Lindner, H. W. Schneider, R. Fawzi, U. Englert and W. Hiller, *Z. Naturforsch., B: Chem. Sci.*, 1988, **43**, 1598.
- 18 J. H. Rivers, L. J. D. Anderson, C. M. N. Starr and R. A. Jones, *Dalton Trans.*, 2012, **41**, 5401.
- 19 A. S. Hock, R. R. Schrock and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2006, **128**, 16373.
- 20 H. Lee, J. B. Bonanno, B. M. Bridgewater, D. G. Churchill and G. Parkin, *Polyhedron*, 2005, **24**, 1356.
- 21 H. F. Klein and H. H. Karsch, *Chem. Ber.*, 1972, **105**, 2628.
- 22 J. Heinicke, N. Peulecke, M. K. Kindermann and P. G. Jones, *Z. Anorg. Allg. Chem.*, 2005, **631**, 67.
- 23 J. Leroy, D. Cantacuzene and C. Wakselman, *Synthesis*, 1982, 313.
- 24 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.
- 25 O. Dahl, *Acta Chem. Scand.*, 1969, **23**, 2342.
- 26 Z. Otwinowski and W. Minor, DENZO-SMN, in *Methods in Enzymology: Macromolecular Crystallography, Part A*, ed. C. W. J. Carter, M. I. Simon and R. M. Sweet, Academic Press, 1997, vol. 276, p. 307.
- 27 G. H. Sheldrick, *SHELX 97, A software package for the solution and refinement of X-ray data*, University of Göttingen, Göttingen, Germany, 1997.
- 28 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2A.