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N-Heterocyclic Carbene Complexes of Rhodium and Iridium: Steric Effects on Molecular Conformation

Gary S. Nichol,*[a] Jonathan Rajaseelan,[b] Laura J. Anna,[c] and Edward Rajaseelan[c]

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A series of new Rh^I triazole-based N-heterocyclic carbene (NHC) complexes [(cod)Rh(NHC)Cl] **2a–c** were obtained by transmetallation from Ag^I complexes using *n*-butyl, benzyl and neopentyl NHC wing tip substituents. The corresponding new Rh^I ionic complexes (**3a-c**) were synthesized by treating compounds **2a–c** with triphenylphosphane and $AgBF_4$. These complexes were characterized by nmr spectroscopy and the structures of **2c**, **3a**, **3b**, and **3c** were determined by single-crystal X-ray diffraction. Compound **3b** formed two polymorphs, the first reported incidence of polymorphism in this type of NHC. Ir analogues, **4**, of complexes **3a–c** were also synthesized; two complexes are isomorphous with the Rh analogues **4b** and **4c** while **4a** has a different structure. Differences in *syn* and *anti* molecular conformation of the NHC ligands is rationalized in terms of stabilizing intramolecular C–H···π interactions and steric crowding of the PPh_3 ligand.

Introduction

N-Heterocyclic carbenes (NHCs)[1–3] have emerged as universal spectator ligands and as alternatives for phosphanes in transition-metal compounds. The first metal–NHC complexes were reported in 1968 by Wanzlick and Schönherr[4] and by Öfele[5] and the first stable free carbenes were isolated in 1991 by Arduengo et al.[6,7] They form strong bonds to metal centers[8–12] and this makes them particularly beneficial in their use as ligands in organometallic catalysts. Contemporary NHC research is both vigorous and diverse; the chemistry of NHC complexes is the frequently the subject of review articles[13–18] and metal-NHC complexes of many transition elements have been reported.

Although the majority of reported NHC research concerns complexes with 1,3-disubstituted imidazolin-2-ylidene-derived ligands,[19] more recent work indicates further exploration of the enormous possibilities afforded by 1,2,4-triazole-derived compounds,[20] including homo- and hetero-binuclear modes of coordination.[21] The area of research, however, remains largely unexplored. A search of the Cambridge Structural Database (CSD; February 2009 update[22]) for all metal complexes with 1,3-disubstituted imidazolin-2-ylidene-derived ligands binding in normal coordination mode (i.e. coordinated through C2) yields 1558 structures. By contrast the same search using 2,4-disubstituted triazole-derived ligands returns just 45 structures, the first a chiral palladium complex reported by Enders et al. in 1996.[23]

We are interested in further examination of triazole-based metal–NHC complexes of Rh and Ir. Steric tuning of NHCs is possible by changing the R^1 and R^2 "wing tip" substituents at N and previous studies have indicated[24–28] the barrier to metal–NHC bond rotation is largely steric in nature. Rh complexes with several NHC ligands have been synthesized and their electronic properties studied.[19,29–31] We report here the synthesis and crystallographic characterization of a series of Rh complexes **2a–c** with general formula [(cod)Rh(NHC)Cl] and the corresponding ionic complexes **3a–c** with general formula $[(cod)Rh(NHC)PPh_3]^+[BF_4]^-$ (cod = cyclooctadiene). Ir analogues of complexes **3a–c** have proven to be very active for transfer hydrogenation of C=C, C=N, and C=O bonds.[20,32] Although the synthesis of Ir analogues has been reported their crystal structures have not and so for the purpose of comparison we also include here the crystal structures of the ionic Ir complexes $[(cod)Ir(NHC)PPh_3]^+[BF_4]^-$ **4a–4c**.

Results and Discussion

Compounds 2a–2c

The compounds [(cod)Rh(NHC)Cl], [NHC = 4-benzyl-1-butyltriazol-5-ylidene (**2a**), 4-butyl-1-neopentyltriazol-5-ylidene(**2b**), 4-benzyl-1-neopentyltriazol-5-ylidene (**2c**)]

[a] Department of Chemistry and Biochemistry, The University of Arizona,
1306 E University Boulevard, Tucson, AZ 85721, USA
Fax: +1-520-621-8407
E-mail: gsnichol@e-mail.arizona.edu
[b] Lancaster Country Day School,
Lancaster, PA 17603, USA
[c] Department of Chemistry, Millersville University,
Millersville, PA 17551, USA

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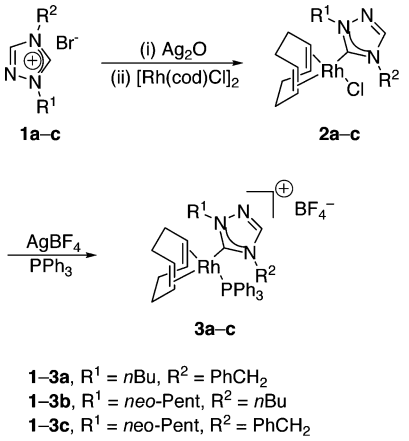
were synthesized by in situ transmetallation from the corresponding Ag carbene complexes as shown in Scheme 1. The triazolium salts **1a**–**c** were treated with Ag_2O in room temperature, the silver-carbene complex formed readily reacted with $[Rh(cod)Cl]_2$ to yield yellow metal carbene compounds **2a**–**c**. These were crystallized from CH_2Cl_2/pentane to give [(cod)Rh(NHC)Cl] in good yield.



Scheme 1. General reaction procedure for Rh complexes.

All of the isolated complexes lack the C5-H triazole proton resonance and show a signal for C3-H triazole proton in the 7.68–7.86 ppm region. The structure of **2c** was determined by single-crystal X-ray diffraction (Figure 1). The compound crystallized as a CH_2Cl_2 solvate and crystallographic refinement data for this and all Rh compounds are summarized in Table 1. Bond lengths and angles are as expected for an Rh–NHC complex. The two wing tips are oriented in a sterically-favoured *anti* arrangement with re-

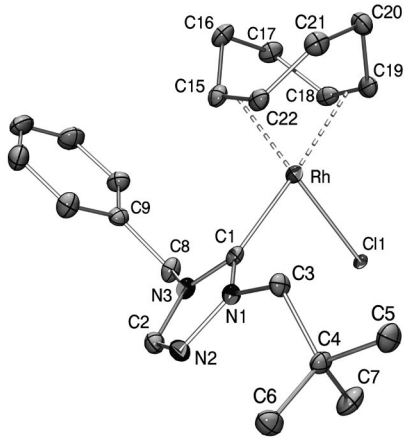


Figure 1. The structure of **2c**. Displacement ellipsoids are at the 50% probability level with hydrogen atoms and solvent CH_2Cl_2 omitted. Selected bond lengths [Å] and angles [°]: Rh–Cl1 2.4143(7), Rh–C1 2.017(3), Rh–C15 2.118(3), Rh–C18 2.187(3), Rh–C19 2.220(3), Rh–C22 2.109(3), N1–C1 1.339(4), N3–C1 1.370(4); Cl1–Rh–C1 88.09(8), N1–C1–N3 102.6(3).

Table 1. Summary of crystallographic data for **2c** and **3a**–**3c**.

Compound	**2c**	**3a**	**3b-1**	**3b-2**	**3c**
Chemical formula	$C_{22}H_{31}ClN_3Rh{\cdot}CH_2Cl_2$	$C_{39}H_{44}N_3PRh^+{\cdot}BF_4^-$	$C_{37}H_{48}N_3PRh^+{\cdot}BF_4^-$	$C_{37}H_{48}N_3PRh^+{\cdot}BF_4^-$	$C_{40}H_{46}N_3PRh^+{\cdot}BF_4^-$
Formula weight	560.78	775.46	755.47	755.47	789.49
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1$	orthorhombic, $Pca2_1$	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, *b*, *c* [Å]	10.664(3)	9.7209(5)	17.5796(17)	9.5515(8),	11.1111(7)
	11.0892(14)	17.2947(8)	10.7382(10)	18.8196(19)	13.0077(7)
	12.1804(16)	11.2937(5)	18.8487(17)	20.417(2)	13.3407(8)
α, *β*, *γ* [°]	116.310(2)	90	90	90	87.6235(12)
	101.264(3)	111.2997(8)	90	101.769(2)	80.4352(13)
	101.292(3)	90	90	90	75.4087(12)
Cell volume [Å^3]	1199.2(4)	1769.00(15)	3558.1(6)	3593.0(6)	1840.00(19)
Z	2	2	4	4	2
Calculated density [g/cm^3]	1.553	1.456	1.410	1.397	1.425
Absorption coefficient μ [mm^{-1}]	1.062	0.582	0.576	0.571	0.561
Crystal color	yellow	yellow	orange	yellow	yellow
Crystal size [mm]	0.26×0.15×0.09	0.28×0.19×0.16	0.24×0.24×0.14	0.31×0.13×0.07	0.27×0.18×0.07
h, *k*, *l*	–13 to 11	–12 to 12	–23 to 22	–4 to 11	–14 to 13
	–8 to 13	–22 to 23	–11 to 14	–23 to 23	–17 to 8
	–15 to 10	–14 to 15	–13 to 24	–25 to 25	–17 to 17
Reflections collected	9795	9829	13399	44684	16537
Independent reflections	5015 (R_{int} = 0.0224)	7758 (R_{int} = 0.0236)	6473 (R_{int} = 0.0435)	7428 (R_{int} = 0.0774)	8725 (R_{int} = 0.0239)
Reflections with $F^2>2\sigma$	4440	7321	5401	5143	7426
Structure solution	direct methods	direct methods	Patterson synthesis	Patterson synthesis	Patterson synthesis
Data/restraints/parameters	5015/0/274	7758/1/444	6473/1/429	7428/31/439	8725/0/500
Final *R* indices	R_1 = 0.0343	R_1 = 0.0295	R_1 = 0.0410	R_1 = 0.0352	R_1 = 0.0330
[$F^2>2\sigma$]	wR_2 = 0.0895	wR_2 = 0.0659	wR_2 = 0.0887	wR_2 = 0.0655	wR_2 = 0.0762
R indices (all data)	R_1 = 0.0406	R_1 = 0.0325	R_1 = 0.0535	R_1 = 0.0738	R_1 = 0.0427
	wR_2 = 0.0930	wR_2 = 0.0674	wR_2 = 0.0953	wR_2 = 0.0792	wR_2 = 0.0803
Goodness-of-fit on F^2	1.048	1.017	1.007	1.049	1.030
Abs. structure parameter[46]		0.269(18)	–0.04(3)		
Largest and mean shift/su	0.001 and 0.000	0.001 and 0.000	0.001 and 0.000	0.001 and 0.000	0.001 and 0.000
Largest diff. peak and hole [e Å^{-3}]	1.61 and –0.50	0.61 and –0.38	0.76 and –0.66	0.62 and –0.61	1.39 and –0.34

spect to one-another, such that the phenyl ring is adjacent to the cod ring and the neopentyl group is oriented away from the cod ring. The crystal packing contains no appreciable C–H···Cl interactions and the crystals were observed to lose solvent CH_2Cl_2 slowly when removed from the mother liquor, causing complete breakdown of the crystal structure integrity overnight.

Compounds 3a and 3c

The corresponding ionic compounds **3a**–**c** were made by treating **2a**–**c** with 1 equiv. of triphenylphosphane and $AgBF_4$ in CH_2Cl_2 in the dark under N_2. The mixture was stirred for 1 h, followed by filtration through Celite and removal of solvent under vacuum to yield yellow-orange solids **3a**–**c** in high yield. In the ^{31}P NMR of the compounds **3a**–**c**, the signal due to the triphenylphosphane ligand was found in the 24.76–24.99 ppm region and the ^{31}P coupling to ^{103}Rh was observed with a coupling constant of 152.77–153.41 Hz. The compounds were crystallized from CH_2Cl_2/pentane and were air stable both as solids and in solution. X-ray crystal structures were obtained for all three compounds. Compound **3b** formed two concomitant polymorphs, discussed below.

The structures of **3a** and **3c** are shown in Figures 2 and 3. The change from Cl^- to PPh_3 as ligand has a negligible effect on Rh–NHC bonding (in **2c** and **3a** both Rh–C distances refine to the same value) and a small but consistent lengthening of the Rh–cod bond lengths. The two structures provide an interesting contrast in the effect of substituent size on wing-tip orientation. In **3a** the flexible *n*-butyl group is in an essentially planar, extended conformation and is *anti* with respect to the benzyl wing tip; the position of the benzyl group appears to be supported by inter- and intramolecular C–H···π interactions (see Figure S1 in the Supporting Information). In **3c** the wing tip substituents are *syn* with respect to one-another. Although this may be ascribed in **3c** to the bulkier and constrained neopentyl group, the *syn* arrangement in **3c** is in stark contrast to the *anti* arrangement in **2c**, a complex with the same NHC ligand but with a Cl^- rather than PPh_3 as the third ligand. An overlay of **2c** and **3c** (Figure 4) shows that not only are the wing tip substituents *syn* in **3c** and *anti* in **2c** but in **3c** the Rh–C1 bond, and hence the entire NHC ligand, is rotated by almost 180° with respect to the remainder of the complex. Substituting the small Cl^- with the significantly larger PPh_3 creates in **3c** steric restrictions to molecular conformation which are not present in **2c**. Furthermore although not adopting a molecular embrace the crystal packing of **3c** is stabilized by C–H···π interactions (Figure S2), as is the orientation of the benzyl ring, so rotation of the Rh–P bond would probably prevent optimum formation of these secondary intra- and intermolecular interactions.

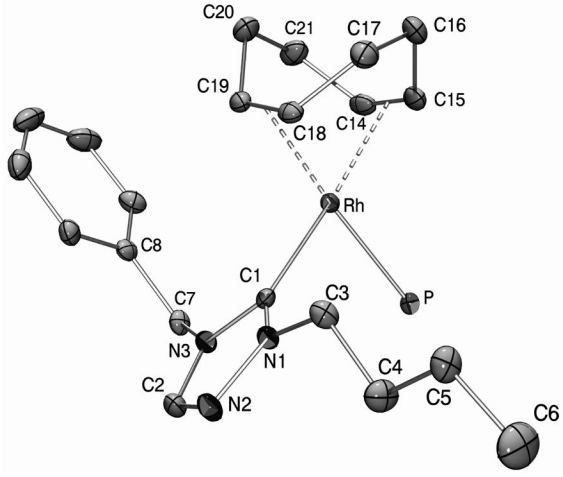


Figure 2. The structure of the complex cation in **3a**. Displacement ellipsoids are at the 50% probability level with PPh_3 phenyl rings and all hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Rh–P 2.3251(7), Rh–C1 2.017(3), Rh–C14 2.224(3), Rh–C15 2.234(3), Rh–C18 2.207(3), Rh–C19 2.240(3); P–Rh–C1 88.20(8), N1–C1–N3 102.6(2).

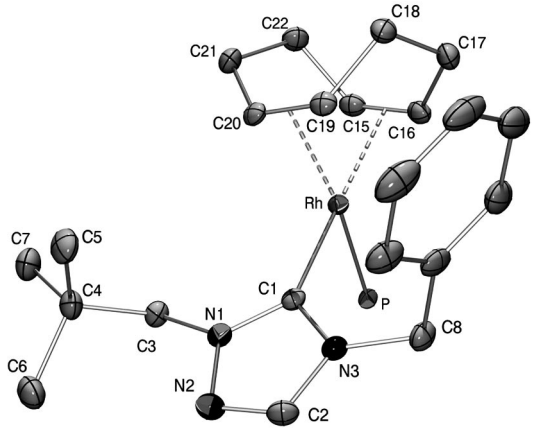


Figure 3. The structure of the complex cation in **3c**. Displacement ellipsoids are at the 50% probability level with PPh_3 phenyl rings and all hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Rh–P 2.3162(6), Rh–C1 2.034(2), Rh–C15 2.215(2),Rh–C16 2.200(2), Rh–C19 2.235(2), Rh–C20 2.180(2); P–Rh–C1 89.50(6), N1–C1–N3 102.27(18).

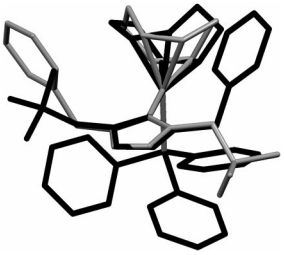


Figure 4. An overlay of **2c** (gray) and **3c** (black) formed by overlaying C1, Rh and P/Cl (rms deviation 0.0408 Å).

Compounds 3b-1 and 3b-2

As compounds **3a** and **3c** have shown the NHC ligand will not necessarily adopt the same conformation in each structure and the final result is one which best optimizes several aromatic stabilising interactions. Compound **3b** has

no phenyl substituent on the NHC ligand, eliminating the C–H···π stabilization seen in **3a** and **3c**, but instead contains a flexible *n*-butyl group and the more constrained neopentyl group. Compound **3b** was crystallized in the same manner as all other compounds in this series. Dark orange block crystals were the first to crystallize (**3b-1**) followed some time later by yellow lath crystals (**3b-2**). Single crystal diffraction data were collected on both crystals which turned out to be two solvent-free polymorphs. The structure of **3b-1** is shown in Figure 5 and the structure of **3b-2** is shown in Figure 6. In **3b-1** the NHC substituents are *anti* and in **3b-2** they are *syn*. Furthermore as with **2c** and **3c** the two polymorphs differ in that the Rh–C bond is rotated by approximately 180°. The conformation of the *n*-butyl group is also different: in **3b-1** it is in a partly closed conformation whereas in **3b-2** the group is both fully extended and exhibits static disorder with a refined major:minor occupancy ratio of 72:28%. There are no significant changes in the bonding of either polymorph.

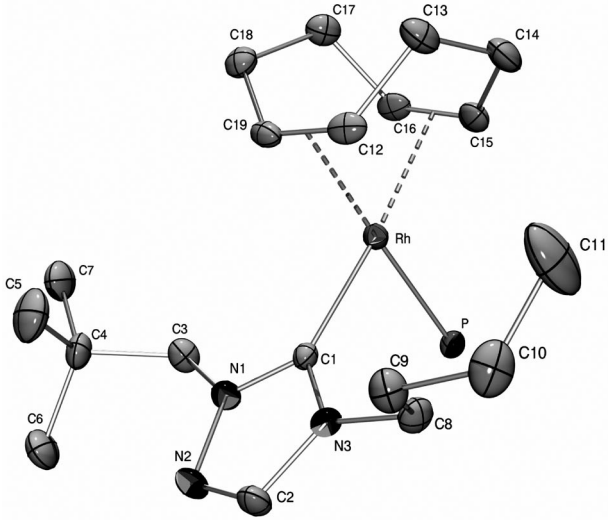


Figure 5. The structure of the complex cation in **3b-1**. Displacement ellipsoids are at the 50% probability level with PPh_3 phenyl rings and all hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Rh–P 2.3199(12), Rh–C1 2.019(4), Rh–C12 2.210(4),Rh–C15 2.211(5), Rh–C16 2.208(4), Rh–C19 2.216(4); P–Rh–C1 88.64(12), N1–C1–N3 103.6(4).

An overlay (Figure 7) again highlights similarities and differences between these two polymorphs. Both cod ligands overlay very closely and although there are some differences in the position of the phenyl rings there is no major discrepancy in the orientation of the two groups of P–C bonds (i.e. neither structure differs significantly by rotation of the Rh–P bond). On the NHC ligand the orientation of the closed *n*-butyl group of **3b-1** closely matches that of the neopentyl group of **3b-2** while obviously on the opposite side of the ligand the two substituents have quite different orientations necessitated by the *anti* and *syn* relationships in both structures.

Unlike **2c** and **3c** the rationale for the two different conformations **3b-1** and **3b-2** is less easily explained by way of maximizing crystal packing interactions. There are no

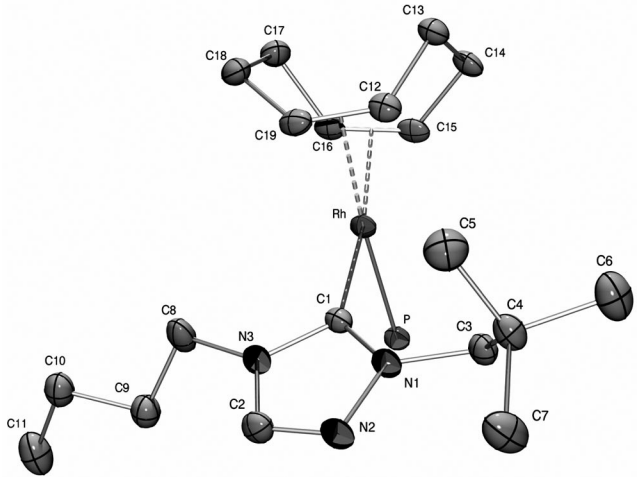


Figure 6. The structure of the complex cation in **3b-2**. Displacement ellipsoids are at the 50% probability level with PPh_3 phenyl rings and all hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Rh–P 2.3261(8), Rh–C1 2.034(3), Rh–C12 2.196(3),Rh–C15 2.217(3), Rh–C16 2.227(3), Rh–C19 2.207(3); P–Rh–C1 91.17(9), N1–C1–N3 103.2(3).

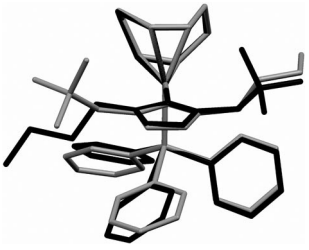


Figure 7. An overlay of **3b-1** (gray) and **3b-2** (black) formed by overlaying C1, Rh and P (rms deviation 0.0356 Å).

intramolecular C–H···π interactions to direct molecular conformation and indeed there are no C–H···π interactions between adjacent PPh_3 groups in the crystal packing of either structure. Comparing **3b-1** and **3c** (Figure S3, Supporting Information) shows that this time there is rotation by approximately 60° about the Rh–C bond such that the PPh_3 ligand in **3b-1** and **3b-2** has a different orientation (relative to the NCH ligand) from **3a** and **3c**. So from a crystal packing point of view there is no obvious explanation as to why two polymorphs have formed. Of course this also means that there is no explanation or reason why two (or more) polymorphs *should not* form in the absence of any significant stabilising intra- or intermolecular interactions. As stated earlier several studies have shown that the barrier to NHC rotation is largely steric in nature. In solution it is clear that the Rh–C bond in **3b** rotates freely. Although the neopentyl group provides some steric hindrance the *n*-butyl group does not, and neither organic group cause as much steric hindrance as a benzyl ring which, in conjunction with PPh_3 may effectively lock the compound into one orientation in solution. Furthermore the attractive intramolecular forces offered by the presence of a phenyl ring are also not

found in **3b**; free rotation of the Rh–P bond to alleviate steric crowding of either neopentyl or *n*-butyl with PPh_3 is quite possible in **3b** but not in **3a** or **3c**. Since the Rh–C bond has little barrier to rotation in solution then it is possible that crystallization of **3b** may yield two different crystal packing arrangements which are similar in energy and so both form as concomitant polymorphs.

It was observed that the orange crystals **3b-1** formed first and the yellow crystals **3b-2** grew subsequently. It could be assumed that the orange crystals are the kinetic product of crystallization and the yellow crystals are the thermodynamic product of crystallization. Although **3b-1** has a slightly higher calculated crystal density and is in a crystal system of higher symmetry; it has crystallized in the noncentrosymmetric space group $Pca2_1$. The value of the absolute structure parameter indicates the correctness of this space group although there is no molecular reason why the compound should have crystallized without a center of symmetry. We noted, however, that the dark orange crystals slowly disappeared over approximately two months of standing at room temperature in a sealed vial, with a larger amount of pale yellow crystals forming. After three months the solvent had mostly evaporated and the majority of the residual crystalline solid was yellow, with two or three small dark orange clusters. Several unit cell redeterminations consistently showed the yellow crystals to match **3b-2** and careful removal of an orange crystal revealed a unit cell which matched **3b-1**. The slow rate of interconversion however suggests that neither polymorph is energetically favoured with any great significance.

To the best of our knowledge this is the only reported example of polymorphism of an NHC complex using an NHC based on either 1,3-disubstituted imidazolin-2-ylidene- or 1,2-disubstituted 4-triazole-derived ligands. A search of the CSD for both of these basic NHC skeletons, with any type of metal bound in normal or abnormal mode, together with the CSD "polymorph" flag set results in no hits. Polymorphism of *N*,*N*′-disubstituted imidazolium salts is a little better known, usually in the context of the structures of ionic liquids; the ionic liquid 1-butyl-3-methylimidazolium chloride, for example, has five reported polymorphs (at different temperatures).[33–36] Temperature-induced *anti*/*syn* polymorphism has also been reported in the compound tris(2-iodo-1,3-dimethoxyimidazolium) chloride bis(hexafluorophosphate) in which the room-temperature structure all three imidazolium cations have methoxy substituents in the *syn* arrangement but cooling to 233 K flips one of the methoxy groups such that one imidazolium adopts an *anti* arrangement.[37] Temperature-induced polymorphism is highly unlikely in any of the structures reported in this manuscript as the changes in molecular conformation necessary to flip from *syn* to *anti* or vice versa involve too many atoms and would doubtless lead to some sort of fatal physical damage to the crystal. This was confirmed by checking the unit cell parameters of each compound, measuring data at room temperature. Except for the expected slight of all unit cell lengths, and a mild increase in unit-cell volume consistent with room-temperature determination, no significant change indicative of temperature-induced polymorphism was found.

Ir Complexes

Ir analogues of compounds **3a** to **3c** were also synthesized and their crystal structures determined; we refer to these Ir compounds as **4a** to **4c**, respectively. Compounds **4b** and **4c** are isomorphous with **3b-1** and **3c** discussed earlier; indeed the coordinates of the Rh compounds were used to solve the Ir analogue structures. With the exception of expected lengthening of unit-cell parameters there is no significant structural change between Rh and Ir in these compounds. A summary of the crystallographic experimental results is given in Table 2 and we shall not repeat structural analysis for these Ir compounds. It is, of course, worth discussing potential polymorphism of **4b** because this was observed in **3b**. In **4b**, however, only one type of crystal was observed to form. These were large dark red block crystals found to be isomorphous with the orthorhombic polymorph **3b-1**. In discussing **3b** we observed very slow conversion of **3b-1** to monoclinic **3b-2**. Compound **4b** was also allowed to stand, undisturbed, for two months. In this case the mother liquor did not completely evaporate yet the crystals showed no obvious morphology change nor was the colour any different. Unit-cell redeterminations matched **4b** and no crystal yielding a monoclinic unit cell was found. On the basis of this observation, and the very slow rate of interconversion of **3b-1** to **3b-2** then it is likely that both polymorphs are indeed very similar in energy and without a seed crystal of the anticipated monoclinic form **4b-2** present in the sample vial there is perhaps no energetic benefit to spontaneous interconversion.

Compound 4a

Compound **4a** proved to be the most difficult of all to crystallize and several attempts were needed. Finally two types of crystal morphology were obtained, rods and blocks, both of which have the same unit-cell dimensions. Compound **4a** is not isomorphous with **3a** and is the only ionic complex to crystallize as a solvate. CH_2Cl_2 is present in the crystal structure; one of the Cl atoms lies on a crystallographic twofold axis and the molecule was modelled as disordered about this axis such that the complex is formally a hemisolvate structure. Consistency of unit-cell determinations indicate that the solvent is present in both crystal morphologies. Furthermore, crystals of this compound exhibit unusual temperature-sensitive behaviour. Flash-cooling to 100 K produces a diffraction pattern with many reflections, particularly at higher Bragg angles, split over two or three positions. It is possible to index the data, yielding multiple domains which have no systematic relationship to one-another (i.e. a 180° rotation about some logical crystallographic axis or direction); the structure is solved easily from a Patterson map but refinement using a multiple-reflection data file (the SHELXL HKLF5 format) does not

Table 2. Summary of crystallographic data for **4a**–**4c**.

Compound	**4a**	**4b**	**4c**
Chemical formula	$C_{39}H_{44}IrN_3P^+\cdot BF_4^-\cdot 0.5CH_2Cl_2$	$C_{37}H_{48}IrN_3P^+\cdot BF_4^-$	$C_{40}H_{46}IrN_3P^+\cdot BF_4^-$
Formula weight	907.21	844.76	878.78
Temperature [K]	200(2)	100(2)	100(2)
Crystal system, space group	monoclinic, *C*2/*c*	orthorhombic, $Pca2_1$	triclinic, $P\bar{1}$
a, *b*, *c* [Å]	18.3487(15) 19.5378(17) 21.2798(17)	17.5522(16) 10.7421(10) 18.9030(17)	11.1299(7) 13.0279(8) 13.3661(8)
α, *β*, *γ* [°]	90 103.842(2) 90	90 90 90	87.5297(11) 80.1767(12) 75.5470(12)
Cell volume [Å^3]	7407.1(11)	3564.1(6)	1849.2(3)
Z	8	4	2
Calculated density [g/cm^3]	1.627	1.574	1.578
Absorption coefficient μ [mm^{-1}]	3.774	3.842	3.706
Crystal color	red	red	red
Crystal size [mm]	0.47 × 0.16 × 0.08	0.21 × 0.17 × 0.13	0.25 × 0.23 × 0.09
h, *k*, *l*	–24 to 24, –24 to 26, –28 to 28	–23 to 23, –9 to 14, –25 to 23	–14 to 11, –17 to 14, –17 to 17
Reflections collected	39809	28402	12820
Independent reflections	9217 (R_{int} = 0.0288)	8436 (R_{int} = 0.0319)	9060 (R_{int} = 0.0163)
Reflections with $F^2>2\sigma$	7684	7355	8307
Structure solution	Patterson synthesis	Patterson synthesis	direct methods
Data/restraints/parameters	9217/4/512	8436/1/429	9060/146/500
Final *R* indices [$F^2>2\sigma$]	R_1 = 0.0247, *wR*2 = 0.0554	R_1 = 0.0263, *wR*2 = 0.0565	R_1 = 0.0245, *wR*2 = 0.0578
R indices (all data)	R_1 = 0.0345, *wR*2 = 0.0598	R_1 = 0.0342, *wR*2 = 0.0594	R_1 = 0.0286, *wR*2 = 0.0593
Goodness-of-fit on F^2	1.006	1.031	1.045
Abs. structure parameter		–0.018(5)	
Largest and mean shift/su	0.004 and 0.000	0.002 and 0.000	0.001 and 0.000
Largest diff. peak and hole [e Å^{-3}]	1.62 and –0.90	0.84 and –0.74	1.55 and –0.58

converge satisfactorily, nor does refinement on just one component of the diffraction pattern. Warming the crystal to 200 K does not give this problem of splitting and the data are easily indexed. Data were measured at 270 K, 200 K, 100 K and then finally again at 270 K. At each temperature the data are indexed to give the same unit cell (in multiple domains at 100 K) but the final 270 K dataset was easily indexed, suggesting this process is reversible. The crystal showed no physical signs of stress, cracking etc., when removed from the diffractometer. We present here structural results from data measured at 200 K.

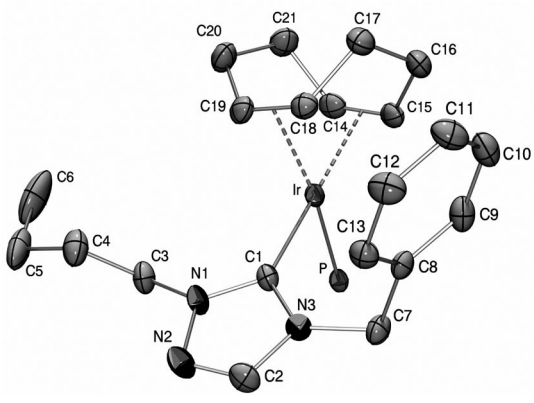


Figure 8. The structure of the complex cation in **4a**. Displacement ellipsoids are at the 50% probability level with PPh_3 phenyl rings, solvent CH_2Cl_2 and all hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Ir–P 2.3137(8), Ir–C1 2.029(3), Rh–C14 2.195(3), Ir–C15 2.184(3), Ir–C18 2.221(3), Ir–C19 2.186(3); P–Ir–C1 90.17(8), N1–C1–N3 102.4(2).

The structure of **4a** is shown in Figure 8. The *n*-butyl group has a partly closed conformation in common with **3b-1** and in contrast to **3a** where it is fully extended. The two wing-tip substituents adopt a *syn* relationship, again in contrast to **3a**, although in this instance the effect of solvent CH_2Cl_2 on the conformation of the *n*-butyl group must be taken into account since the two are adjacent in space. Much like the **3b** polymorphs, compounds **3a** and **4a** also differ in that the Ir–C bond is rotated by approximately 180° (Figure S4, Supporting Information) although in common with all other benzyl-containing wing-tip compounds the orientation of the benzyl ring is stabilized by a favorable C–H···π interaction from the cod ligand.

Conclusions

We have reported on the structural variation observed in a systematic series of Rh and Ir NHC compounds. A range of different molecular conformations are possible, depending on the steric bulk of the wing-tip substituents used and also any further intramolecular stabilization such substituents provide. In all structures using a benzyl substituent the compound is seen to adopt a conformation which allows for stabilization by C–H···π bonding from the cod ligand. The effect of the PPh_3 ligand is also important because it adds extra steric restrictions to an already crowded complex.

Structures **3b-1** and **3b-2** are, to the best of our knowledge, the first example of polymorphism of an NHC complex using an NHC based on either 1,3-disubstituted imid-

azolin-2-ylidene- or 1,2-disubstituted 4-triazole-derived ligands. The slow interconversion of one polymorph to another, coupled with the apparent lack of observed polymorphism of the Ir compound, suggest that although one set of crystals were observed to grow first the difference in energy between the kinetic and thermodynamic products of crystallization must be quite small. It is worth noting, however, that the lack of observed polymorphism in compound **4b** should not be taken as evidence that **3b-1** and **3b-2** represent an isolated incident. As **4a** shows it should not be assumed that merely changing the metal centre to the next element down in that particular group of the periodic table will always yield isomorphous crystalline products. If polymorphism of **3b** is possible then one cannot discount the possibility that, of the hundreds of reported NHC compounds for which a crystal-structure determination was made, and especially those which contain relatively small or flexible wing tip substituents, then in some cases the crystal chosen was not representative of the bulk sample and polymorphism was overlooked.

Experimental Section

General Methods: 1-Butyl-1,2,4-triazole,[38] 1-neopentyl-1,2,4-triazole,[39] 4-benzyl-1-butyltriazolium bromide,[20] 4-butyl-1-neopentyltriazolium bromide,[20] and 4-benzyl-1-neopentyltriazolium bromide[20] were synthesized as described previously. All other compounds used in the synthesis were obtained from Aldrich and Strem and were used as received. All subsequent synthesis were performed in air (unless otherwise noted), using reagent grade solvents, which were used as received without further purification.

Isolated yields are given for all products. NMR spectra were recorded at room temperature in $CDCl_3$ with a 400-MHz (operating at 162 MHz for ^{31}P) Varian Spectrometer and referenced to the residual solvent peak (δ in ppm and J in Hz). Elemental analyses were performed by Atlantic Microlab, Inc. The Ir analogues of complexes **3a**–**c** were synthesized as previously reported,[20] recrystallized by slow diffusion of pentane into a CH_2Cl_2 solution and their structures were also determined by single-crystal X-ray diffraction.

Transmetallation Reactions. General Procedure: A suspension of the appropriate triazolium bromide (**1a**–**c**; 1 equiv.) and silver oxide (0.5 equiv.) was stirred at room temperature in the dark for 1.5 h. Then the mixture was filtered through Celite (to remove unreacted silver oxide and any insoluble residues) and the resulting mixture was stirred with $[Rh(cod)Cl]_2$ (0.5 equiv.) in the dark for 1.5 h. The formation of a white precipitate was observed, and the suspension was filtered through Celite to remove the silver salts, and the solvent was removed under reduced pressure. The resulting solid was dried under vacuum and crystallized from CH_2Cl_2/pentane.

(4-Benzyl-1-butyltriazol-5-ylidene)chlorido[(1,2,5,6-η)-1,5-cyclooctadiene]rhodium (2a): Transmetallation was carried out in 15 mL of dichloromethane with **1a** (254 mg, 0.84 mmol), Ag_2O (101 mg, 0.44 mmol), and $[Rh(cod)Cl]_2$ (208 mg, 0.44 mmol). The product was a bright yellow solid; yield 380 mg(97%). ^1H NMR: δ = 7.68 (s, 1 H, NC_3HN), 7.40–7.36 (m, 5 H, H_{arom}), 5.78 (m, 2 H, CH_{cod}), 5.12 (s, 2 H, CH_2Ph), 4.62 (m, 2 H, CH_{cod}), 4.30 [m, 2 H, CH_2(Bu)], 3.36–3.22 [m, 2H $(CH_2)_{cod}$], 2.42 [m, 2 H, $(CH_2)_{cod}$], 2.30 [m, 2 H, $(CH_2)_{cod}$], 2.10 [m, 2 H, $(CH_2)_{cod}$], 1.93 [m, 2 H, CH_2(Bu)], 1.49 [m, 2 H, CH_2(Bu)], 1.04 [t, $^3J_{H\text{-}H}$ = 8.4 Hz, 3 H, CH_3(Bu)] ppm. ^{13}C NMR: δ = 185.46 (d, $J_{Rh\text{-}C}$ = 51.56 Hz, Rh-C), 141.82 (NC_3HN), 134.95, 129.26, 128.74, 128.52, 128.45 (C_{arom}), 98.77, 99.57, 68.81, 68.73, (CH_{cod}), 52.61 (CH_2Ph), 52.51 [NCH_2(Bu)], 32.91, 32.83 [$(CH_2)_{cod}$], 31.96 [CH_2(Bu)], 28.91, 28.74 [$(CH_2)_{cod}$], 19.99 [CH_2(Bu)], 13.78 [CH_3(Bu)] ppm. $C_{21}H_{29}ClN_3Rh$ (461.83): calcd. C 54.61, H 6.33, N 9.09; found C 54.42, H 6.24, N 8.89.

(4-Butyltriazole-1-neopentyl-5-ylidene)chlorido[(1,2,5,6-η)-1,5-cyclooctadiene]rhodium (2b): Transmetallation was carried out in 15 mL of dichloromethane with **1b** (160 mg, 0.58 mmol), Ag_2O (67 mg, 0.29 mmol), and $[Rh(cod)Cl]_2$ (143 mg, 0.29 mmol). The compound was a bright yellow solid; yield 231 mg(90%). ^1H NMR: δ = 7.86 (s, 1 H, NC_3HN), 4.61 [m, 2 H, NCH_2(Bu)], 4.51 (m, 2 H, CH_{cod}), 4.38 (m, 2 H, CH_{cod}), 4.14 (s, 2 H, CH_2CMe_3), 2.42 [m, 2 H, $(CH_2)_{cod}$], 2.36 [m, 2 H, CH_2(Bu)], 2.05, 2.02, 1.91 [m, 6 H, $(CH_2)_{cod}$], 1.48 (m, 2 H, CH_2Me), 1.13 (s, 9 H, CCH_3), 1.05 [t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3 H, CH_3(Bu)] ppm. ^{13}C NMR: δ = 186.03 (d, $J_{Rh\text{-}C}$ = 51.40 Hz, Rh-C), 141.42 (NC_3HN), 99.15, 99.01, 69.08, 68.08 (CH_{cod}), 63.65 (CH_2CMe_3), 48.58 [NCH_2(Bu)], 33.48, 32.81 [(CH_2)cod], 32.54 (CH_2CMe_3), 32.20 [CH_2(Bu)], 29.51, 28.72 [$(CH_2)_{cod}$], 28.29 [$C(CH_3)_3$], 20.06 (CH_2CH_3), 13.75 [CH_3(Bu)] ppm. $C_{19}H_{33}ClN_3Rh$ (441.84): calcd. C 51.65, H 7.53, N 9.51; found C 51.20, H 7.43, N 9.22.

(4-Benzyl-1-neopentyltriazol-5-ylidene)chlorido[(1,2,5,6-η)-1,5-cyclooctadiene]rhodium (2c): Transmetallation was carried out in 15 mL of dichloromethane with **1c** (406 mg, 1.31 mmol), Ag_2O (152 mg, 0.65 mmol) and $[Rh(cod)Cl]_2$ (322 mg, 0.65 mmol). The compound was a bright yellow solid; yield 584 mg(94%). ^1H NMR: δ = 7.70 (s, 1 H, NC_3HN), 7.39–7.26 (m, 5 H, H_{arom}), 5.80 (m, 2 H, CH_{cod}), 5.06 (s, 2 H, CH_2CMe_3), 4.69 (m, 1 H, CH_{cod}), 4.22 (m, 1 H, CH_{cod}), 3.24 (s, 2 H, CH_2Ph), 2.44–2.23 [m, 4 H, $(CH_2)_{cod}$], 2.02–1.87 [m, 4 H, $(CH_2)_{cod}$], 1.15 (s, 9 H, CCH_3) ppm. ^{13}C NMR: δ = 186.59 (d, $J_{Rh\text{-}C}$ = 50.86 Hz, Rh-C), 141.65 (NC_3HN), 135.11–128.43 (C_{arom}), 99.54, 99.38, 69.51, 68.01 (CH_{cod}), 63.67 (CH_2CMe_3), 52.57 (CH_2Ph), 33.38 (CH_2CMe_3), 32.88, 32.21, 29.49 [$(CH_2)_{cod}$], 28.88, 28.75, 28.21 (CCH_3) ppm. $C_{22}H_{31}ClN_3Rh$ (475.86): calcd. C 55.53, H 6.57, N 8.83; found C 55.09, H 6.49, N 8.85.

General Procedure for the Synthesis of Complexes 3a–c: A suspension of the appropriate complex **2a**–**c** (1 equiv.), triphenylphosphane (1 equiv.), and $AgBF_4$ (1 equiv.) in CH_2Cl_2 was stirred at room temperature in the dark for 1.5 h under nitrogen. The immediate formation of a white precipitate was observed. Then the mixture was filtered through Celite to remove silver chloride and any insoluble residues. The solvent was removed from the filtrate under reduced pressure. The residue was washed thoroughly with pentane and dried under vacuum. The resulting solids were recrystallized from CH_2Cl_2/pentane,

(4-Benzyl-1-butyltriazol-5-ylidene)[(1,2,5,6-η)-1,5-cyclooctadiene]-triphenylphosphanerhodium(I) Tetrafluoroborate (3a): Triphenylphosphane (171 mg, 0.65 mmol), and $AgBF_4$ (127 mg, 0.65 mmol) were added to **2a** (300 mg, 0.65 mmol) in 15 mL of degassed dichloromethane. The product was a bright orange solid; yield 490 mg(97%). ^1H NMR: δ = 7.94 (s, 1 H, NC_3HN), 7.53–7.30 (m, 20 H, H_{arom}), 5.30 (s, 2 H, CH_2Ph), 5.42, 5.38, 4.84, 4.80 (m, 4 H, CH_{cod}), 4.45 [m, 2 H, NCH_2(Bu)], 2.35 [m, 5 H, $(CH_2)_{cod}$], 2.17 [m, 2 H, CH_2(Bu)], 2.03 [m, 3 H, $(CH_2)_{cod}$], 1.33 (m, 2 H, CH_2Me), 0.90 [t, $^3J_{H\text{-}H}$ = 7.6 Hz, 3 H, CH_3(Bu)] ppm. ^{13}C NMR: δ = 181.98 (d, $J_{Rh\text{-}c}$ = 46.90 Hz, Rh-C), 143.97 (NC_3HN), 133.66–128.23 (C_{arom}), 99.51, 97.56, 96.76, 94.56 (CH_{cod}), 52.86 [NCH_2(Bu)], 52.24 (CH_2Ph), 30.85, 30.29 [$(CH_2)_{cod}$], 30.12 [CH_2(Bu)], 20.08 (CH_2Me), 13.72 [CH_3(Bu)] ppm. ^{19}F NMR: δ = –153.37 ppm. ^{31}P NMR: δ = 24.99 (d, $J_{Rh\text{-}P}$ =

152.77 Hz) ppm. $C_{39}H_{44}BF_4N_3PRh$ (775.47): calcd. C 60.40, H 5.72, N 5.42; found C 59.95, H 5.73, N 5.24.

(4-Butyl-1-neopentyltriazol-5-ylidene)[(1,2,5,6-η)-1,5-cyclooctadiene]-triphenylphosphanerhodium(I) Tetrafluoroborate (3b): Triphenylphosphane (118 mg, 0.45 mmol), and $AgBF_4$ (88 mg, 0.45 mmol) were added to **2b** (201 mg, 0.45 mmol) in 10 mL of degassed dichloromethane. The product was a bright orange-red solid; yield 310 mg(91%). ^{1}H NMR: δ = 8.13 (s, 1 H, NC_3HN), 7.51–7.25 (m, 15 H, H_{arom}), 4.88 (s, 2 H, CH_2CMe_3), 4.44 [m, 2 H, NCH_2(Bu)], 4.22, 3.89, 3.07 (m, 4 H, CH_{cod}), 2.48, 2.25 [m, 6 H, $(CH_2)_{cod}$], 2.18 [m, CH_2(bu)], 1.63 [m, 2 H, $(CH_2)_{cod}$], 1.39 (m, 2 H, CH_2Me), 1.01 (s, 9 H, CCH_3), 0.94 [t, $^3J_{H\text{-}H}$ = 7.2 Hz, 3 H, CH_3(Bu)] ppm. ^{13}C NMR: δ = 182.30 (d, $J_{Rh\text{-}C}$ = 36.50 Hz, Rh-C), 143.45 (NC_3HN), 133.48–129.09 (C_{arom}), 95.38, 95.31, 94.60, 94.53 (CH_{cod}), 63.41 (CH_2CMe_3), 48.77 [NCH_2(Bu)], 32.32 (CH_2CMe_3), 31.75, 30.88, 30.27 [$(CH_2)_{cod}$], 29.86 [CH_2(Bu)], 27.04 (CCH_3), 20.08 (CH_2Me), 13.67 [CH_3(Bu)] ppm. ^{19}F NMR: δ = –153.58 ppm. ^{31}P NMR: δ = 24.93 (d, $J_{Rh\text{-}C}$ = 153.41 Hz) ppm. $C_{37}H_{48}BF_4N_3PRh$ (755.48): calcd. C 58.82, H 6.40, N 5.56; found C 58.27, H 6.37, N 5.28.

(4-Benzyl-1-neopentyltriazol-5-ylidene)[(1,2,5,6-η)-1,5-cyclooctadiene]-triphenylphosphanerhodium(I) Tetrafluoroborate (3c): Triphenylphosphane (142 mg, 0.54 mmol), and $AgBF_4$ (106 mg, 0.54 mmol) were added to **2c** (258 mg, 0.54 mmol) in 15 mL of degassed dichloromethane. The product was a bright orange solid; yield 402 mg (94%). ^{1}H NMR: δ = 7.85 (s, 1 H, NC_3HN), 7.75–7.27 (m, 20 H, H_{arom}), 5.48, 5.65, 4.97, 4.68 (m, 4 H, CH_{cod}), 5.30 (s, 2 H, CH_2CMe_3), 4.74 (s, 2 H, CH_2Ph), 3.20, 2.45–1.28 [m, 8 H, $(CH_2)_{cod}$], 1.02 (s, 9 H, CCH_3) ppm. ^{13}C NMR: δ = 182.99 (d, $J_{Rh\text{-}C}$ = 62.50 Hz, Rh–C), 143.88 (NC_3HN), 134.88–128.01 (C_{arom}), 96.21, 94.15 (CH_{cod}), 52.55 (CH_2CMe_3), 52.28 (CH_2Ph), 34.13 (CH_2CMe_3), 32.37, 30.48, 28.75 [$(CH_2)_{cod}$], 28.54 (CCH_3) ppm. ^{19}F NMR: δ = –153.08 ppm. ^{31}P NMR: δ = 24.76 (d, $J_{Rh\text{-}P}$ = 152.77 Hz) ppm. $C_{40}H_{46}BF_4N_3PRh$ (789.50): calcd. C 60.85, H 5.87, N 5.32; found C 60.30, H 5.82, N 5.12.

X-ray Crystallography: Single-crystal X-ray diffraction data were collected with a Bruker Kappa APEXII DUO CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). For all experiments the crystal temperature was maintained at 100 K or 200 K using an Oxford Cryosystems Cryostream 700.[40] Programs used were: data collection, APEX2;[41] data reduction, SAINT;[42] face-indexed absorption correction, SADABS;[43] structure solution and refinement, SHELXTL;[44] molecular graphics, ORTEP-3 for Windows.[45] For all structures hydrogen atoms were placed geometrically and then refined using a riding model with U_{iso}(H) = 1.5U_{eq}(C) for methyl and U_{iso}(H) = 1.2U_{eq}(C) for all other hydrogen atoms. C–H distances were fixed in the range 0.95–1.00 Å depending on the parent carbon. Two-part disorder models were used for **3b-2** (butyl group), **3c**, **4a** and **4c** (each BF_4^-) with refined major:minor occupancy ratios of 72:28, 55:45, 55:45 and 57:43% respectively.

CCDC-733196 (for **2c**), -733197 (for **3a**), -733198 (for **3b-1**), -733199 (for **3b-2**), -733200 (for **3c**), -733201 (for **4a**), -733202 (for **4b**), -733203 (for **4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Tables with bond lengths, angles and torsion angles for each compound.

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[1] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.
[2] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.
[3] T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.
[4] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.
[5] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42–P43.
[6] A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
[7] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[8] K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, *J. Organomet. Chem.* **1993**, *459*, 177–184.
[9] W. A. Herrmann, K. Öfele, M. Elison, F. E. Kühn, P. W. Roesky, *J. Organomet. Chem.* **1994**, *480*, C7–C9.
[10] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419.
[11] J. Schwarz, V. P. W. Böhm, M. G. Gardinger, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschal-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780.
[12] M. Bortenschlager, J. Schütz, D. von Preysing, O. Nuyken, W. A. Herrmann, R. Weberskirch, *J. Organomet. Chem.* **2005**, *690*, 6233–6237.
[13] S. T. Liddle, I. S. Edworthy, P. L. Arnold, *Chem. Soc. Rev.* **2007**, *36*, 1732–1744.
[14] S. Wurtz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523–1533.
[15] R. H. Crabtree, *Coord. Chem. Rev.* **2007**, *251*, 595.
[16] S. P. Nolan, *Eur. J. Inorg. Chem.* **2009**, 1664.
[17] O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, DOI: 10.1021/cr8005087.
[18] J. M. Praetorius, C. M. Crudden, *Dalton Trans.* **2008**, 4079–4094.
[19] W. A. Herrmann, J. Schütz, G. D. Frey, E. Hertweck, *Organometallics* **2006**, *25*, 2437–2448.
[20] D. Gnanamgari, A. Moores, E. Rajaseelan, R. H. Crabtree, *Organometallics* **2007**, *26*, 1226–1230.
[21] E. Mas-Marz, J. A. Mata, E. Peris, *Angew. Chem. Int. Ed.* **2007**, *46*, 3729–3731.
[22] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388.
[23] D. Enders, H. Gielena, G. Raabea, J. Runsink, J. H. Teles, *Chem. Ber.* **1996**, *129*, 1483–1488.
[24] M. J. Doyle, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 679–680.
[25] W. A. Herrmann, L. J. Goossen, M. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357–366.
[26] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493.
[27] D. Enders, H. Gielen, *J. Organomet. Chem.* **2001**, *617*, 70–80.
[28] J. A. Mata, A. R. Chianese, J. R. Miecznikowski, M. Poyatos, E. Peris, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 1253–1263.
[29] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461–2468.
[30] S. Douglas, J. P. Lowe, M. F. Mahon, J. E. Warren, M. K. Whittlesey, *J. Organomet. Chem.* **2005**, *690*, 5027–5035.
[31] H. Sato, T. Fujihara, Y. Obora, M. Tokunaga, J. Kiyoso, Y. Tsuji, *Chem. Commun.* **2007**, 267–271.
[32] A. M. Voutchkova, D. Gnanamgari, C. E. Jakobsche, C. Butler, S. J. Miller, J. Parr, R. H. Crabtree, *J. Organomet. Chem.* **2008**, *693*, 1815–1821.

[33] J. Kaerkkaeinen, J. Asikkala, R. S. Laitinen, M. K. Lajunen, *Z. Naturforsch. Teil B* **2004**, *59*, 763–770.
[34] P. Kölle, R. Dronskowski, *Inorg. Chem.* **2004**, *43*, 2803–2809.
[35] S. Saha, S. Hayashi, A. Kobayashi, H.-o. Hamaguchi, *Chem. Lett.* **2003**, *32*, 740–741.
[36] J. D. Holbrey, W. M. Reichert, M. Nieuwenhuyzen, S. Johnson, K. R. Seddon, R. D. Rogers, *Chem. Commun.* **2003**, 1636–1637.
[37] G. Laus, A. Schwarzler, P. Schuster, G. Bentivoglio, M. Hummel, K. Wurst, V. Kahlenberg, T. Lorting, J. Schutz, P. Peringer, G. Bonn, G. Nauer, H. Schottenberger, *Z. Naturforsch. Teil B* **2007**, *62*, 295–308.
[38] E. Diez-Barra, A. De la Huz, R. I. Rodriguez-Curiel, J. Tejeda, *Tetrahedron* **1997**, *53*, 2253–2260.
[39] J. A. Mata, E. Peris, C. Incarvito, R. H. Crabtree, *Chem. Commun.* **2003**, 184–185.
[40] J. Cosier, A. M. Glazer, *J. Appl. Crystallogr.* **1986**, *19*, 105–107.
[41] APEX2, Bruker AXS, Madison, Wisconsin, USA, **2007**.
[42] SAINT, Bruker AXS, Madison, Wisconsin, USA, **2007**.
[43] SADABS, G. M. Sheldrick, University of Göttingen, Germany, **1996**.
[44] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[45] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[46] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

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