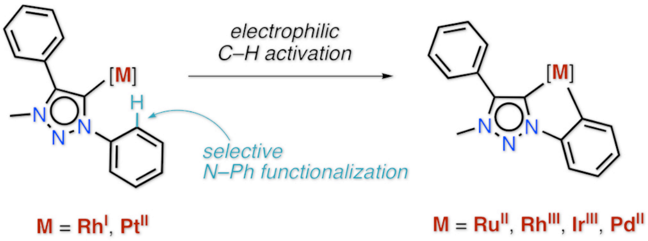
Title	Regioselective Electrophilic C-H Bond Activation in Triazolylidene Metal Complexes Containing a N-Bound Phenyl Substituent
Authors(s)	Donnelly, Kate F., Lalrempuia, Ralte, Müller-Bunz, Helge, Albrecht, Martin
Publication date	2012-11-29
Publication information	Donnelly, Kate F., Ralte Lalrempuia, Helge Müller-Bunz, and Martin Albrecht. “Regioselective Electrophilic C-H Bond Activation in Triazolylidene Metal Complexes Containing a N-Bound Phenyl Substituent.” American Chemical Society, November 29, 2012. https://doi.org/10.1021/om300983m.
Publisher	American Chemical Society
Item record/more information	http://hdl.handle.net/10197/6594
Publisher's statement	This document is the unedited author's version of a Submitted Work that was subsequently accepted for publication in Organometallics, copyright © American Chemical Society after peer review. To access the final edited and published work, see http://pubs.acs.org/doi/abs/10.1021/om300983m.
Publisher's version (DOI)	10.1021/om300983m

Regioselective electrophilic C–H bond activation in triazolylidene metal complexes containing a *N*-bound phenyl substitutent

Kate F. Donnelly, Ralte Lalrempuia, Helge Müller-Bunz, Martin Albrecht*

School of Chemistry & Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

Phone: +353-17162504; Fax: +353-17162501; Email: martin.albrecht@ucd.ie



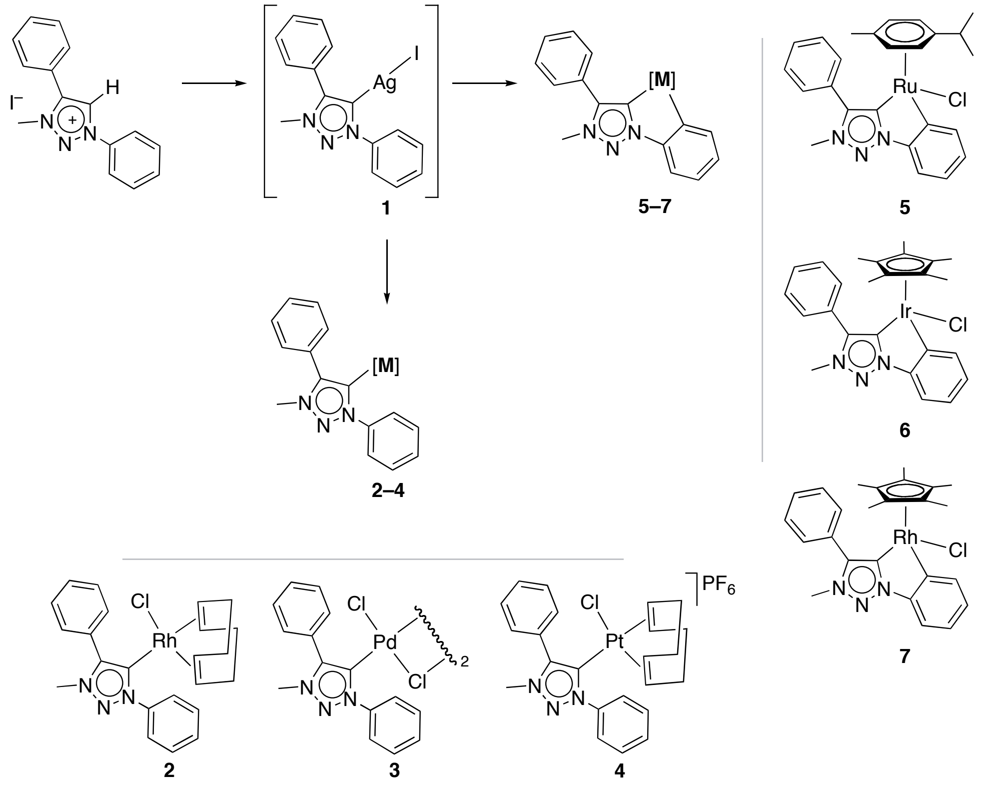
Summary: Transmetalation of 1,4-diphenyl-substituted 1,2,3-triazolylidene silver complex with an electrophilic metal center, e.g., Ru^{II}*, Ir*^{III}*, or Rh*^{III}*, induces spontaneous and chemoselective cyclometalation involving C–H bond activation of the N-bound phenyl group exclusively. Less electrophilic metals such as Ir*^{I}*, Rh*^{I}*, and Pt*^{II} *yield a monodentate triazolylidene complex, while cyclometalation with borderline cases (Pd*^{II}*) or the activation of the C-bound phenyl ring required acetate as a promoter.*

Cyclometalation has become a useful concept for stabilizing reactive M–C bonds through chelation,[1] thus enabling exploitation of organometallic entities for materials science and catalysis.[2] Moreover, cyclometalation provides a versatile route for the directed activation of relatively inert C–H and C–R bonds, which has spurred the development of mild procedures for the functionalization of aromatic and aliphatic hydrocarbon units.[3] Typically, cyclometalation is a two-step process that involves initial binding of a directing group to the metal center and subsequent metal-mediated C–H bond activation and C–M bond formation to close the metallacycle.[1,4] Classical directing groups include heteroatom donors, which bind the metal reversibly. Carbon donors have recently gained relevance, a development that has been promoted in particular by the discovery of N-heterocyclic carbenes (NHCs) as powerful ligands for transition metals.[5] For example, Arduengo-type carbenes that contain an aryl wingtip group as *N*-substituent form metallacycles through C–H bond activation when bound to a late transition metal such as ruthenium, palladium or platinum,[6] and this process has also been accounted for the deactivation of derivatives of Grubbs' 2nd generation olefin metathesis catalysts.[7]

Cyclometalation via wingtip C–H bond activation has been incidentally observed with other carbenes. For example, triazolylidene ligands—an easily accessible and emerging subclass of NHCs[8]—have been shown to undergo cyclometalation when bound to palladium(II)[9] or iridium(III).[10] In preliminary investigations, we and others noted that the acetate-induced cyclopalladation of triazolylidenes involved the *N*-bound phenyl group specifically.[9] Stimulated by these initial observations, we have investigated the cyclometalation reaction in more detail. Here we report on the extension of the cyclometalation to various other platinum group metals, and on the basic trends that govern the C–H bond activation process in phenyl wingtip groups.[11]

Previous work established that transmetalation of the presumably monomeric carbene silver complex **1** with rhodium(I) or palladium(II) affords complexes **2** and **3**, respectively,[9a] comprising a monodentate triazolylidene (trz) complex (Scheme 1). Expansion of this methodology to different metal centers yielded complexes **4–7**. Platinum complex **4** is a cationic version of complex **2** and features a monodentate triazolylidene ligand and a cod spectator ligand. Exchange of the non-coordinating anion during the synthesis of **4** from chloride to PF_6^- enhanced the solubility of the complex and thus facilitated analysis and reactivity studies. In contrast to the clean triazolylidene transfer observed with platinum(II), transmetalation with $[RuCl_2(cym)]_2$ as ruthenium(II) precursor induced spontaneous C–H bond activation of one of the phenyl substituents and afforded the cyclometalated complex **5** with a C_{trz},C_{Phe}-bidentate bonding mode of the triazolylidene ligand.[12] An identical reaction outcome was observed when using $[IrCl_2(Cp^*)]_2$ or $[RhCl_2(Cp^*)]_2$ as metal precursor for the generation of the metallacyclic complexes **6** and **7**.

Scheme 1



Cyclometalation occurred chemoselectively and involved the *N*-substituted phenyl group exclusively. Highly selective C_{Ph}–H bond activation was indicated by the clean NMR spectrum that revealed only a single isomer. Specifically, the presence of four distinct signals for the aromatic protons in the low-field region of the ^{1}H NMR spectrum demonstrates desymmetrization of the *N*-bound phenyl group. In addition, two low-field ^{13}C NMR resonances were observed, *e.g.* at $\delta_C = 173.0$ (C_{trz}) and 166.3 (C_{Ph}) for the ruthenium metallacycle **5**. A nuclear Overhauser effect (NOE) between the methyl group bound to N3 ($\delta_H = 4.10$ ppm) and the doublet at $\delta_H = 7.91$ due to the *ortho* protons of the *C*-bound phenyl ring unambiguously indicated that this phenyl ring is unaffected and that cyclometalation occurred at the *N*-bound phenyl group exclusively.

The monodentate bonding mode in the triazolylidene platinum complex **4** was readily identified in the ^{1}H NMR spectrum by the two sets of multiplets for the phenyl *ortho* protons at equal integral ratio, and a multiplet for the *meta* and *para* protons. Based on NOE experiments, the high-field doublet at $\delta_H = 8.17$ was assigned to the C-bound phenyl ring and the more shielded set at 7.95 ppm was accordingly attributed to the phenyl group bound to the heterocyclic nitrogen. The olefinic protons of the cod ligand are split into a lowfield multiplet (2H) and two multiplets at higher field (1H each). The highfield signals display well resolved coupling to ^{195}Pt with a coupling constant ($J_{PtH} = 62$ Hz) similar to that in [$PtCl_2$(cod)] ($J_{PtH} =$ 66.4 Hz), thus suggesting a *trans* positioned chloride ligand. In contrast, the Pt–H coupling is only poorly resolved in the lowfield resonance, and from the broadening of the socket of the signal, a coupling constant smaller than 40 Hz may be inferred. This small coupling constant is in agreement with the high *trans* influence attributed to these mesoionic triazolylidene ligands. As expected for a planar chiral system, , a desymmetrization of the phenyl nuclei was observed in the ^{13}C NMR spectrum (*cf* multiplets for the *ortho* phenyl protons in ^{1}H NMR spectroscopy). The platinum-bound carbon resonates at 144.2 ppm ($^1J_{PtC}$ not resolved).

The connectivity patterns deduced from NMR spectroscopic analyses were unambiguously confirmed by single crystal X-ray diffraction analysis of complex **2** as well as the new complexes **4–6**. Thus, the molecular structure of complexes **2** and **4** features a square-planar metal center bound to the cod ligand, a chloride, and the monodentate triazolylidene ligand (Fig. 1a, b). In both complexes, the olefinic carbons *trans* to chloride are about 0.07 Å closer to the metal center than when bound *trans* to the triazolylidene ligand. A similar *trans* influence was observed with Arduengo-type NHCs.[13] In complexes **5** and **6**, the triazolylidene ligand is bidentate chelating via the N–bound phenyl group (Fig. 1c,d). The bite-angle is 78° in both complexes, and the M–C$_{Ph}$ bond is about 0.05 Å longer than the M–C$_{trz}$ bond.[14] The M–C$_{trz}$ bond length is not significantly affected by the bidentate bonding mode and falls within the 1.99–2.04 Å range for all four complexes. Nonetheless, chelation has distinct structural implications. A pronounced yaw distortion[15] was noted for the chelating systems (13.56° and 13.14° for **5** and **6**, respectively), while the corresponding distortion is much smaller in the monodentate complexes (< 3.2° in complexes **2** and **4**). In addition, the triazolylidene plane coincides with the planar metallacycle, as indicated by the negligibly small dihedral angles. In contrast, the triazolylidene ligand is strongly twisted out of the coordination square plane of rhodium and platinum in complexes **2** and **4** (dihedral angles between 67° and 81°).

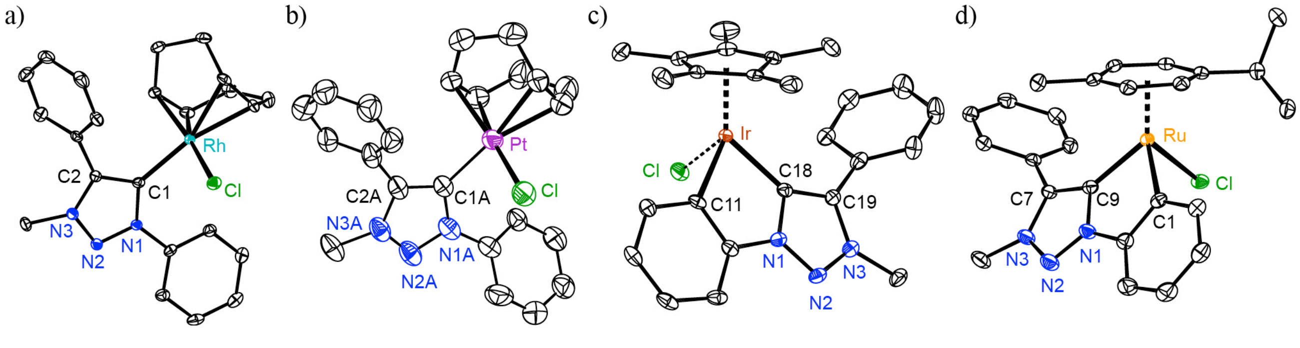
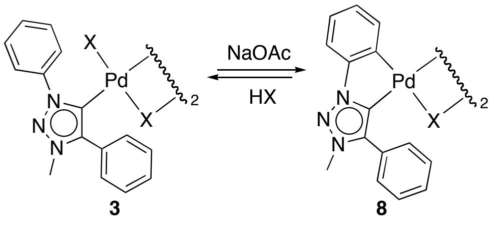


Fig. 1 ORTEP plots of complexes **2** (a), **4** (b; only one of the two disordered conformations shown), **5** (c), and **6** (d), all at 50% probability, hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (deg) for complexes **2**, **4**, **5**, and **6**.

complex	**2** (M = Rh)	**4** (M = Pt) A	**4** (M = Pt) B	**5** (M = Ru)	**6** (M = Ir)
M–Cl	2.3841(4)	2.3026(19)	2.3026(19)	2.4208(3)	2.4935(5)
M–C$_{trz}$	2.0390(16)	1.991(10)	2.031(11)	2.0372(15)	2.013(2)
M–C$_{COD}$	2.1051(16)	2.155(7)	2.155(7)	---	---
M–C$_{COD}$	2.1178(16)	2.172(8)	2.172(8)	---	---
M–C$_{COD}$	2.1839(17)	2.232(9)	2.232(9)	---	---
M–C$_{COD}$	2.1971(17)	2.266(9)	2.266(9)	---	---
M–C$_{Ph}$	---	---	---	2.0831(15)	2.055(2)
C$_{trz}$–M–C$_{Ph}$	---	---	---	77.79(6)	78.32(10)
C$_{trz}$–M–Cl	---	---	---	88.16(4)	87.81(7)
C$_{Ph}$–M–Cl	---	---	---	88.31(4)	88.26(7)
N1–C$_{trz}$–M	132.26(12)	127.2(11)	130.8(10)	115.57(11)	115.71(18)
C$_{trz}$–C$_{trz}$–M	125.87(12)	127.7(10)	124.8(11)	142.69(11)	141.98(19)
Cl–M–C$_{trz}$–N1	–75.16(14)	–67(2)	110(3)	1.64(11)	–2.42(18)
Cl–M–C$_{trz}$–C$_{trz}$	99.54(13)	102(3)	–73(3)	178.91(19)	175.2(3)

Attempts to promote cyclometalation included the reaction of the monodentate complexes **2–4** with OAc$^-$ as a privileged proton scavenger.[16] However, the rhodium complex **2** and the platinum analogue **4** were inert under a variety of different reaction conditions (coordinating or non-coordinating solvent, RT or elevated temperature), even when using AgOAc as a combined potential proton and halide scavenger. Reactions were also carried out in CD_3OD to monitor transient cyclometalation, though no deuterium incorporation into either of the phenyl substituents was identified. In contrast, the palladium triazolylidene complex **3** cleanly underwent cyclopalladation in the presence of NaOAc at room temperature to produce complex **8** (Eq. 1),[9a] *i.e.* the palladium analogue of complexes **5–7**.

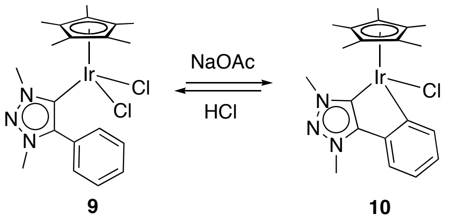


3 **8**

(1)

The metallacycles in complexes **5–7** were remarkably robust. No ring opening was observed when any of these complexes was treated with HCl in methanol (RT, 24 h). Likewise, no deuterium incorporation was detected upon reaction of complexes **5–7** in DCl/*i*PrOD–D_8 at reflux for a short period of time (10 min). Upon prolonged heating, slow decomposition was noted as the only reactivity pattern. In contrast, chelation in the palladacycle **8** is unstable under acidic conditions and reverts to the monodentate species **2**.

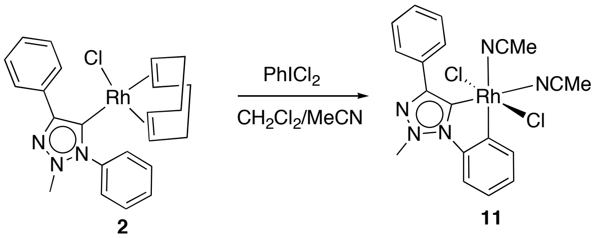
Even though cyclometalation with the diphenyl-substituted triazolylidene precursor is chemoselective and exclusively involves C–H activation of the N-bound phenyl ring, activation of the *C*-bound phenyl group would be possible, in principle. For example, when using a *N,N''*-dimethyl–*C*-phenyl substituted triazolium precursor, cycloiridation was observed in the presence of NaOAc (Eq. 2).[10b] Of note, the primary product of the transmetalation reaction is the monodentate carbene iridium complex **9** and cyclometalation requires prolonged heating in $C_2D_4Cl_2$ compared to the smooth C–H activation of the *N*-bound phenyl group upon formation of **5** already at room temperature. In agreement with the energetically demanding forward reaction, the reverse iridacycle ring opening in **10** is facile and the presence of HCl rapidly restores the monodentate bonding mode.



(2)

The observed reactivity patterns provide some insights into key factors that govern cyclometalation in these triazolylidene metal complexes. Cyclometalation is substantially easier with electron-rich phenyl rings, *i.e.* aniline-type arenes that are bound to the nitrogen of the heterocyclic carbene. In addition, electron-poor metal centers (high-valent Rh^{III}, Ir^{III}, Ru^{II}) spontaneously induce C–H activation, while electron-rich centers (Rh^{I}, Pt^{II}) are resistant to cyclometalation. In addition, acetate assists cyclometalation in borderline cases (Pd^{II}, Ir^{III} if the C-bound phenyl group is involved). These trends are all consistent with an electrophilic bond activation mechanism, as extensively studied both experimentally and theoretically.[17]

Support for this general pattern was obtained by the successful cyclometalation of rhodium when starting from complex **2**. Rather than directly forcing a C–H activation, this complex was stirred in the presence of dichloro(phenyl)iodine(III), which induced rhodium oxidation and spontaneous cyclometalation to give complex **11**. Despite the limited stability of this complex and the formation of detectable amounts of triazolium salt as side product, unambiguous evidence for the formation of **11** was obtained from NMR spectroscopic analysis The ^{1}H NMR spectrum reveals a diagnostic desymmetrization of the N-bound phenyl group into four distinct resonances. Moreover, the phenyl carbon bound to the rhodium center appeared as a doublet at 149.5 ppm ($^1J_{\mathrm{RhC}}$ = 28.9 Hz).



(3)

In conclusion, selective aromatic C–H bond activation of the N–bound phenyl wingtip group in triazolylidenes has been demonstrated to follow an electrophilic pathway. These results suggest that the aniline-type character of the phenyl ring, with the N-substituent as an electron donor, is prevailing over the potentially electron-withdrawing character of the azolium system. The high propensity of the N-phenyl wingtip group to undergo cyclometalation is expected to have implications for catalyst design. Specifically in borderline cases, where cyclometalation is reversible, proton-coupled redox processes may become accessible.

Experimental section

General. All metalation reactions were carried out under strict exclusion of air using standard schlenk techniques. The 3-methyl-1,4-diphenyl triazolium iodide, the triazolylidene complexes **1–3**[9a] and **8–10**,[10b] and the precursor salts [IrCp*Cl$_2$],[18] and [Pt(cod)Cl$_2$][19] were prepared according to literature procedures. All other reagents were commercially available and used as received. NMR spectra were recorded at 25 °C and chemical shifts (δ in ppm and coupling constants J in Hz) were referenced to the protio signal of residual solvent and are reported downfield from SiMe$_4$ (^{1}H, ^{13}C). The ^{19}F NMR shifts are referenced by using the absolute ^{19}F NMR frequency and the field-offset (Z0) of the corresponding NMR solvent. Assignments are based on homo- and heteronuclear correlation spectroscopy. The adopted atom numbering in the cyclometalated started at the metal-bound carbon (C1), circled towards the nitrogen-bound carbon (C2) and finished at C6, the carbon *ortho* to the metal-bound carbon. Elemental Analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland.

Complex 4: Dry CH$_2$Cl$_2$ (18 mL) was added to the triazolium salt (0.108 g, 0.40 mmol) and Ag$_2$O (0.051 g, 0.22 mmol). The reaction mixture was stirred at room temperature for 5 h under inert atmosphere in the dark. The mixture was then diluted with CH$_2$Cl$_2$ and filtered through a pad of Celite. All volatiles were removed in vacuo to afford the silver carbene complex **1** (0.126 g, 0.168 mmol) as a white solid. This residue was immediately added to [Pt(cod)Cl$_2$] (0.126 g, 0.336 mmol) in CH$_2$Cl$_2$ and the solution was stirred at room temperature for 16 h. The reaction mixture was diluted with CH$_2$Cl$_2$ and filtered through Celite twice and then concentrated to ca. 2 mL. Acetone (20 mL) was added followed by addition of KPF$_6$ (0.062 g, 0.328 mmol). A white precipitate immediately formed. The mixture was stirred at room temperature for 3 h and then filtered through Celite, eluting with CH$_2$Cl$_2$ (100 mL) and acetone (25 mL). The filtrates were combined and all volatiles were removed in vacuo, yielding complex **4** as an off-white solid (0.098 g, 40%). An analytically pure sample was obtained by slow diffusion of pentane into a solution of **4** in $CHCl_3$. ^1H NMR (400MHz, $CDCl_3$): NMR (400MHz, $CDCl_3$): δ 8.18–8.16 (m, 2H, $H_{Ph\ ortho}$), 7.96–7.93 (m, 2H, $H_{Ph\ ortho}$), 7.66–7.61 (m, 6H, $H_{Ph\ meta+para}$), 5.88–5.79 (m, 2H, CH_{cod}), 4.71 (td, $^3J_{HH}$ = 3.9 Hz, $^3J_{HH}$ = 7.3 Hz, J_{PtH} = 62 Hz, 1H, CH_{cod}), 4.57 (td, $^3J_{HH\ (alkene)}$ = 3.9 Hz, $^3J_{HH}$ = 7.5 Hz, J_{PtH} = 62 Hz, 1H, CH_{cod}), 4.20 (s, 3H, NCH_3), 2.32–2.12 (m, 6H, $CH_{2\ cod}$), 1.95–1.81 (m, 2H, $CH_{2\ cod}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.2 (C_{trz}–Pt, $^1J_{PtC}$ not resolved), 138.8 (C_{trz}–Ph), 138.4 (N–C_{Ph}), 131.1, 131.0, 130.7, 129.8, 129.4, 126.0, 125.3, 116.0, 115.8 (9 × C_{Ph}), 100.2, 95.5, 93.2 (3 × CH_{cod}), 38.1 (N–CH_3), 31.9, 31.8, 28.5, 28.3 (4 × $CH_{2\ cod}$). ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.14 (d, $^1J_{FP}$ = 713 Hz, PF_6). Anal. Calcd. for $C_{23}H_{25}ClF_6N_3PPt$ (718.96) × 0.5 CH_2Cl_2: C, 37.07; H, 3.44; N, 5.52; P, 4.07; Found C, 36.80; H, 3.13; N, 5.29; P, 4.31.

Complex 5. Dry CH_2Cl_2 (18 mL) was added to the triazolium salt (0.108 g, 0.40 mmol) and Ag_2O (0.051 g, 0.22 mmol). The reaction mixture was stirred at room temperature for 5 h under nitrogen and the exclusion of light. The mixture was diluted with CH_2Cl_2 and filtered through Celite. All volatiles were removed in vacuo to afford the silver carbene (0.122 g, 0.160 mmol) as a white solid. The silver carbene was immediately added to a solution of [Ru(*p*-cymene)Cl_2]$_2$ (0.100 g, 0.160 mmol) in dry CH_2Cl_2 (10 mL) and the solution was stirred at room temperature for 16 h. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. All volatiles were removed in vacuo, the orange residue was washed with pentane and then dissolved in CH_2Cl_2. Pentane was added and the resulting mixture was centrifuged. The supernatant and washings were combined and all volatiles were evaporated, yielding the complex as a brown/orange solid (0.062 g, 31%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H^6), 7.91 (d, $^3J_{HH}$ = 9.6 Hz, 2H, $H_{C\text{-}Ph\ ortho}$), 7.61–7.57 (m, 4H, H^5 + $H_{C\text{-}Ph\ meta+para}$), 7.11 (t, $^3J_{HH}$ = 8.0 Hz, 1H, H^4), 7.01 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H^3), 5.26–5.23 (m, 2H, H_{cym}), 4.83–4.79 (m, 2H, H_{cym}), 4.10 (s, 3H, N–CH_3), 2.13 (sept, $^3J_{HH}$ = 7.2 Hz, 1H, CHMe$_2$), 1.93 (s, 3H, cym–CH$_3$), 0.81, 0.73 (2 × d, $^3J_{HH}$ = 7.2 Hz, 3H, CH–CH_3). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 173.0 (C$_{trz}$–Ru), 166.3 (C$_{Ph}$–Ru), 145.7 (C C$_{trz}$–Ph), 144.9 (C$_{Ph}$–N), 142.0 (C^6), 130.7 (C$_{C\text{-Ph ortho}}$), 129.7, 128.8 (C$_{C\text{-Ph meta, para}}$), 128.7 (C$_{C\text{-Ph ipso}}$), 127.3 (C^5), 122.3 (C^4), 113.8 (C^3), 102.2, 99.7 (2 × C_{cym}–C), 89.7, 89.5, 88.5, 84.4 (4 × C$_{cym}$–H), 37.0 (N–CH$_3$), 30.9 (CHMe$_2$), 23.0 21.5 (2 × CH–CH$_3$), 18.9 (cym–CH$_3$). Anal. Calcd. for $C_{25}H_{26}ClN_3Ru$ (505.01): C, 59.46; H, 5.19; N, 8.32. Found: C, 59.11; H, 5.15; N, 8.23.

Complex 6. Under nitrogen atmosphere, the triazolium salt (0.55 g, 0.20 mmol) and Ag$_2$O (0.025 g, 0.11 mmol) were suspended in dry CH$_2$Cl$_2$ (10 mL), and the reaction mixture was stirred at room temperature for 5 h in the absence of light. The mixture was filtered through Celite onto [IrCp*Cl$_2$]$_2$ (0.080 g, 0.10 mmol). The resulting solution was stirred at room temperature for 16 h. The reaction mixture was subsequently diluted with CH$_2$Cl$_2$ and filtered through Celite. The filtrate was evaporated to dryness in vacuo and the residue was dissolved in CH$_2$Cl$_2$ (3 mL) followed by the addition of pentane (60 mL). The solution was left at 4 °C for 48 h. During this period, a yellow/orange precipitate formed, which was separated by filtration and then re-dissolved in a minimal quantity of CH$_2$Cl$_2$. The solution was filtered through a short pad of silica, eluted with CH$_2$Cl (50 mL), and then with acetone/CH$_2$Cl$_2$ (10:1, 50 mL). All volatiles of the filtrate were removed in vacuo, affording complex **6** as a light orange solid (0.063 g, 52%). Slow diffusion of pentane into a solution of **6** in CH$_2$Cl$_2$ yielded an analytically pure sample. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, H^6), 7.80 (dd, 2H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, H$_{C\text{-Ph ortho}}$), 7.65 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, H^3), 7.57–7.51 (m, 3H, H$_{C\text{-Ph meta+para}}$), 7.13 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, H^5), 7.02 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.0 Hz, H^4), 4.09 (s, 3H, N–CH$_3$), 1.49 (s, 15H, Cp–CH$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 150.2 (C$_{trz}$–Ir), 144.9 (C$_{Ph}$–N), 144.8 (C$_{Ph}$–Ir), 143.7 (C$_{trz}$–Ph), 137.5 (C^6), 130.7 (C$_{C\text{-Ph ortho}}$), 129.6, 128.9 (C$_{C\text{-Ph meta, para}}$), 128.2 (C$_{C\text{-Ph ipso}}$), 121.9 (C^4), 113.5 (C^3), 90.3 (C$_{Cp}$), 36.9 (N–CH$_3$), 9.1 (Cp–CH$_3$). Anal.

Calcd. for $C_{25}H_{27}N_3IrCl$ (716.6) × $CHCl_3$: C, 43.58; H, 3.94; N, 5.86; Found C, 43.51; H, 3.80; N, 6.14.

Complex 7: The triazolium salt (0.088 g, 0.32 mmol), Ag_2O (0.045 g, 0.19 mmol) and $[RhCp^*Cl_2]_2$ (0.10 g, 0.16 mmol) were placed under nitrogen. Dry CH_2Cl_2 (10 mL) was added and the reaction mixture was stirred at room temperature for 18 h under the exclusion of light. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was evaporated to dryness in vacuo. The residue was extracted with Et_2O (3 × 20 mL) and the combined organic fractions were evaporated, thus yielding the product as a yellow solid (83 mg, 50%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.91–7.86 (m, 3H, H^6, $H_{C\text{-Ph ortho}}$), 7.63 (dd, $^3J_{HH}$ =8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H^3), 7.61-7.53 (m, 3H, $H_{C\text{-Ph ortho+meta}}$), 7.19 (td, $^3J_{HH}$ = 8Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H^5), 7.10 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H^4), 4.15 (s, 3H, N–CH_3), 1.41 (s, 15H, Cp–CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 167.5 (d, $^1J_{RhC}$ = 52.1 Hz, C_{trz}–Rh), 161.7 (d, $^1J_{RhC}$ = 35.6 Hz, C_{Ph}–Rh), 145.5 (C_{Ph}–N), 145.3 (C_{trz}–Ph), 138.7 (C^6), 130.6 ($C_{C\text{-Ph ortho}}$), 129.6 ($C_{C\text{-Ph para}}$), 128.8 ($C_{C\text{-Ph meta}}$), 128.2 ($C_{C\text{-Ph ipso}}$), 127.7 (C^5), 122.6 (C^4), 113.4 (C^3), 97.0 (C_{Cp}), 37.2 (N–CH_3), 9.1 (Cp–CH_3). HRMS (ESI^+): *m/z* = 472.1250 $[M–Cl]^+$, calculated for $C_{25}H_{27}N_3Rh$ 472.1260.

Complex 11. Dry CH_2Cl_2 (15mL) was added to dichloro(phenyl)iodine(III) (0.068 g, 0.226 mmol) and **2** (0.052 g, 0.123 mmol) under N_2 atmosphere, and the solution was stirred for 16 h at rt. CH_3CN (2 mL) was added and the reaction was stirred for a further 2 h. All volatiles were removed in vacuo, the residue was washed with Et_2O (3 × 10 mL) and $CHCl_3$ (15 mL). The light yellow solid (0.042 g, 70%) was dried under reduced pressure and stored under nitrogen at 4 °C to minimize decomposition. ^{1}H NMR (400 MHz, CD_3CN) δ 7.89 (d, $^3J_{HH}$ = 8Hz, 1H, H^6), 7.85 (d, $^3J_{HH}$ = 8Hz, 2H, $H_{C\text{-Ph ortho}}$), 7.66–7.60 (m, 4H, H^3 + $H_{C\text{-Ph ortho+meta}}$), 7.20 (t, $^3J_{HH}$ = 8 Hz, 1H, H^5), 7.13 (t, $^3J_{HH}$ = 8 Hz, 1H, H^4), 4.06 (s, 3H, N–CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 149.5 (d, $^2J_{RhC}$ = 28.9Hz, C_{Ph}–Rh), 144.5 (C_{Ph}–N), 144.4 (C_{trz}–Ph), 137.4 (C^6), 131.3 ($C_{C\text{-Ph ortho}}$), 130.1 ($C_{C\text{-Ph para}}$), 128.4 ($C_{C\text{-Ph meta}}$), 127.3 (C^5), 127.1 ($C_{C\text{-Ph ipso}}$), 123.1 (C^4), 113.6 (C^3), 37.4 (N–CH_3), C_{trz}–Rh not resolved. HRMS (ESI$^+$): *m/z* = 454.0297 [M–Cl]$^+$, calculated for $C_{19}H_{18}ClN_5Rh$ 454.0306.

Crystal structure determinations. Crystal data for **2**, **4**, **5**, and **6** were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. **6** was measured with Cu–K_α (1.54184 Å), all others with Mo–K_α (0.71073 Å). An at least complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed for all these crystals.[20] The structures were solved by direct methods using SHELXS-97[21] and refined by full matrix least-squares on F^2 for all data using SHELXL-97. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms.

Further crystallographic details are compiled in the supporting information. CCDC numbers 905706 (**2**), 905705 (**4**), 905704 (**5**) and 905703 (**6**) 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 available: NMR spectra of **7** and **11**, and X-ray crystal data for **2**, **4**, **5**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments: We gratefully acknowledge financial support by the Irish Research Council (fellowship to K.F.D.), Science Foundation Ireland, and the European Research

Council for a starting grant (ERC-StG 208561), and we thank Johnson Matthey for a generous loan of precious metals.

References

(1) (a) Dehand, J., Pfeffer, M., *Coord. Chem. Rev.* **1976**, *18*, 327. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (c) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406. (d) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (e) Djukic, J.-P.; Sortais, J.-B.; Barloy, L.; Pfeffer, M. *Eur. J. Inorg. Chem.* **2009**, 817. (f) Albrecht, M. *Chem. Rev.* **2010**, *110*, 576.

(2) (a) Albrecht, M.; van Koten, G. *Angew. Chem. Int. Ed.* **2001**, *40*, 3750. (b) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (c) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080. (d) Williams, J. A. G. *Chem. Soc. Rev.* **2009**, *38*, 1783. (e) Huang, Z.; White, P. S.; Brookhart, M. *Nature* **2010**, *465*, 598. (f) Choi, J.; Roy, MacArthur, A. H.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761. (g) Choi, J.; Wang, D. Y.; Kundu, S.; Choliy, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *Science* **2011**, *332*, 1545. (h) Albrecht, M.; Lindner, M. M. *Dalton Trans.* **2011**, *40*, 8733.

(3) (a) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (d) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315.

(4) (a) Dunina, V. V.; Gorunova, O. N. *Russ. Chem. Rev.* **2004**, *73*, 309. (b) Vicente, J.; Saura-Llamas, I. *Comments Inorg. Chem.* **2007**, *28*, 39.

(5) (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. (d) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (e) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677. (f) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.

(6) (a) Hiraki, K.; Onishi, M.; Sugino, K. *J. Organomet. Chem.* **1979**, *171*, C50. (b) Hiraki, K.; Sugino, K. *J. Organomet. Chem.* **1980**, *201*, 469. (c) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194. (d) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944. (e)

Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *247*, 2247. (f) Frey, G. D.; Schütz, J.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2005**, *24*, 4416. (g) Stylianides, N.; Danopoulos, A. A.; Pugh, D.; Hancock, F.; Zanotti-Gerosa, A. *Organometallics* **2007**, *26*, 5627. (h) Liu, Z.; Zhang, T.; Shi, M. *Organometallics* **2008**, *27*, 2668. (i) Häller, L. J. L.; Page, M. J.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 4604. (j) G. L. Petretto, M. Wang, A. Zucca, J. P. Rourke, *Dalton Trans.* **2010**, *39* 7822. (k) Tang, C. Y.; Thompson, A. L.; Aldrige, S. *J. Am. Chem. Soc.* **2010**, *132*, 10578.

(7) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(8) (a) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534. (b) Guisado-Barrios, G.; Bouffard, J.; Donnadieu B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 4759. (c) Crowley, J. D.; Lee A.-L.; Kilpin, K. J. *Aust. J. Chem.* **2011**, *64*, 1118.

(9) (a) Poulain, A.; Canseco-Gonzalez, D.; Hynes-Roche, R.; Müller-Bunz, H.; Schuster, O.; Stoeckli-Evans, H.; Neels, A.; Albrecht, M. *Organometallics* **2011**, *30*, 1021. (b) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *Organometallics* **2011**, *30*, 1689.

(10) (a) Lalrempuia, R.; McDaniel, N. D.; Müller-Bunz, H.; Bernhard, S.; Albrecht, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 9765. (b) Petronilho, A.; Rahman, M.; Woods, J. A.; Al-Sayyed, H.; Müller-Bunz, H.; MacElroy, J. M. D.; Bernhard, S.; Albrecht, M. *Dalton Trans.* **2012**, *41*, 13074.

(11) Presented in parts at the XXV International Conference on Organometallic Chemistry, September 2012, Lisbon (abstract F2.23).

(12) The same cycloruthenation has also been reported by Inomata, S.; Ogata, K.; Fukuzawa, S., XXV International Conference on Organometallic Chemistry, September 2012, Lisbon, abstract PB.61.

(13) For examples, see: (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Koecher, C.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 772. (b) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042. (c) Sato, H.; Fujihara, T.; Obora, Y.; Tokunaga, M.; Kiyosu, J..; Tsuji, Y. *Chem. Commun.* **2007**, 269.

(14) (a) Corberan, R.; Sanau, M.; Peris, E. *J. Am. Chem. Soc.* **2006**, *128*, 3974. (b) Corberan, R.; Sanau, M.; Peris, E. *Organometallics* **2006**, *25*, 4002.

(15) Leung, C. H.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2006**, *25*, 6099.

(16) (a) Davies, D. L.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754. (b) Boutadla, Y.; Al-Duaij, O.; Davies, D. L.; Griffith, G. A.; Singh, K. *Organometallics* **2009**, *28*, 433. (c) Boutadla, Y.; Davies, D. L.; Jones, R. C.; Singh, K. *Chem. Eur. J.* **2011**, *17*, 3438.

(17) (a) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132. (b) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Fawcett, J.; Little, C.; Macgregor, S. A. *Organometallics* **2006**, *25*, 5976. (c) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Polleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (d) Garcia-Cuadrado, D.; de Mendoza, P.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc*. **2007**, *129*, 6880. (e) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Am. Chem. Soc*. **2008**, *130*, 10848. (f) Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc*. **2008**, *130*, 16474. (g) Boutadla, Y.; Davies, D. L.; Macgregor S. A.; Poblador-Bahamonde, A. I. *Dalton Trans*. **2009**, 5820. (h) Kefalidis, C. E.; Baudoin O.; Clot, E. *Dalton Trans*. **2010**, *39*, 10528. (i) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749.

(18) Ball, R. G.; Graham, W. A. G.; McMAster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.

(19) Baldwin, J. A.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chim. Acta* **2006**, *359*, 3079.

(20) Spek, A. L. *J. Appl. Cryst*. 2003, **36**, 7.

(21) Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112.