ORGANOMETALLICS

Note

pubs.acs.org/Organometallics

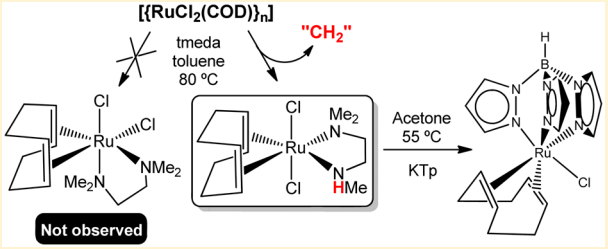
Atom-Economical Synthesis of the Versatile Ruthenium Precursor [TpRuCl(COD)] (Tp = Hydrotris(pyrazol-1-yl)borate) Discloses a Diamine Ligand Dealkylation Process

Manuel Jiménez-Tenorio,* M. Carmen Puerta,* and Pedro Valerga

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica-INBIO, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

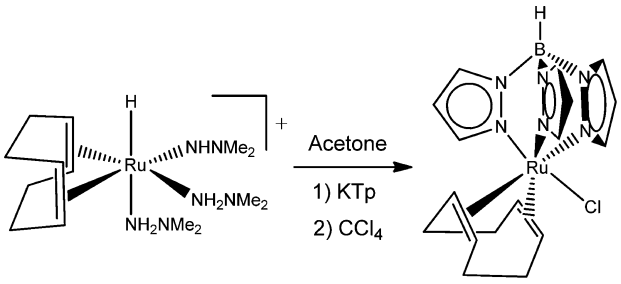
Supporting Information

ABSTRACT: An atom-economical, more environmentally friendly alternative method of synthesis of the versatile complex [TpRuCl(COD)] (**1**) (Tp = hydrotris(pyrazol-1-yl)borate; COD = 1,5-cyclooctadiene) has been developed. Instead of starting from $[RuHCl(COD)(NH_2NMe_2)_3]^+$, **1** can be conveniently prepared by reaction of the derivative *trans*-$[RuCl_2(COD)(Me_2NCH_2CH_2NHMe)]$ (**2**) with KTp in acetone at 55 °C. Compound **2**, which has been structurally characterized by X-ray crystallography, results from an unexpected diamine dealkylation process which takes place in the course of the reaction of $[\{RuCl_2(COD)\}_n]$ with tmeda (tmeda = $Me_2NCH_2CH_2NMe_2$) in toluene at 80 °C. This process had been overlooked in the literature, as compound **2** had been misidentified as *cis*-$[RuCl_2(COD)(tmeda)]$, and suggests that amine dealkylation might occur more commonly than previously anticipated.



The complex [TpRuCl(COD)] (**1**) is a versatile starting material which has been successfully used in the synthesis of many TpRu derivatives, due to the labile character of the COD ligand.[1−8] This compound was originally prepared by reaction of $[RuH(COD)(NH_2NMe_2)_3][PF_6]$[9] with KTp to give the hydrido complex [TpRuH(COD)], which is readily converted into **1** upon treatment with CCl_4 (Scheme 1).[10]

Scheme 1



Carrying out the reaction with $[RuH(COD)(NH_2NMe_2)_3][BPh_4]$ instead of the $[PF_6]^-$ salt improves significantly the yields of **1**.[1] This synthetic procedure involves the use of significant amounts of toxic and carcinogenic 1,1-dimethylhydrazine in the preparation of the parent compound. Furthermore, the 1,1-dimethylhydrazine ligands are released upon reaction with KTp, so there is a generation of dangerous residues which require proper and safe waste disposal. On the other hand, if the $[BPh_4]^-$ salt is used, contaminated deposits of solid $K[BPh_4]$ are produced as byproducts of the reaction. With a current price of more than $500 US per 100 g, $Na[BPh_4]$ turns out to be a rather expensive chemical, which is treated as expendable during the synthesis of **1** by this method, which, although effective, is overall atom-economically inefficient. For this reason, it is advisable to use alternative, more environmentally friendly and atom-economical synthetic procedures for the preparation of **1**. Thus, **1** has been prepared by direct reaction of polymeric $[\{RuCl_2(COD)\}_n]$ with an excess KTp in refluxing THF.[11] However, this procedure has some problems due to formation of mixtures of **1** with the complex $[RuCl_2(COD)(Hpz)]$ resulting from the thermal degradation of unidentified pyrazole-containing materials. **1** has been obtained more recently by reaction of the precursor $[RuCl_2(COD)(MeCN)_2]\cdot H_2O$[12] with KTp in 1,2-dichloroethane or THF, with reported yields ranging from 75% to 87%.[8,13]

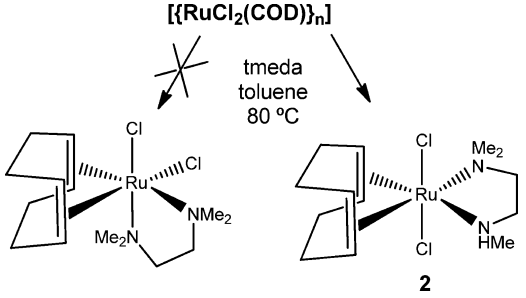
In our search for efficient and safe atom-economical synthetic procedures for the preparation of **1**, we focused our attention on the monomeric compound $[RuCl_2(COD)(tmeda)]$ as a suitable precursor. The isomer *trans*-$[RuCl_2(COD)(tmeda)]$ is prepared by reaction of $CHCl_3$ with the hydride complex *trans*-$[RuHCl(COD)(tmeda)]$, which, in turn, is obtained by treatment of $[\{RuCl_2(COD)_n\}]$ with tmeda in refluxing MeOH.[14] We carried out the reaction of *trans*-$[RuCl_2(COD)(tmeda)]$ with KTp in acetone under reflux over a period of 18 h. After this time, a yellow precipitate of **1** was obtained, which was isolated in a rather moderate yield of 35% upon purification. The isomer *cis*-$[RuCl_2(COD)(tmeda)]$ has been

Received: December 19, 2014
Published: February 24, 2015

DOI: 10.1021/om501307a
Organometallics 2015, 34, 1001−1004

also reported to exist.[15] Mixtures of *cis*- and *trans*-[$RuCl_2$-(COD)(tmeda)] are obtained by reaction of [{$RuCl_2$-$(COD)_n$}] with tmeda in toluene at 80 °C over a period of 24 h. The *cis*- and *trans*-isomers are obtained in a 3:2 ratio, but longer reaction times seem to favor the formation of the *cis*-isomer, which may increase its proportion up to 83% in the composition of the mixture.[15] The reaction of such a mixture of *cis*- and *trans*-[$RuCl_2$(COD)(tmeda)] with KTp in acetone under reflux yielded a yellow precipitate upon stirring for a few minutes. After 1.5−2 h, complex **1** was isolated in ca. 60% yield upon purification. It would appear that the *cis*-[$RuCl_2$(COD)-(tmeda)] isomer is far more reactive than the *trans*-isomer, a fact which would be consistent with reactivity patterns observed in other instances, i.e., in complexes of the type *cis*-/*trans*-[$RuCl_2(PP)_2$] (PP = dppe, dppm).[16] In an attempt to optimize the reaction conditions, we purified the *cis*-[$RuCl_2$(COD)-(tmeda)] isomer by fractional recrystallization from dichloromethane/petroleum ether. The large yellow-orange crystals that were obtained upon recrystallization showed ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2 matching satisfactorily the reported spectroscopic data for the alleged *cis*-[$RuCl_2$(COD)(tmeda)].[15] Interestingly, the IR spectrum of these crystals exhibits one sharp band at 3218 cm^{-1}. X-ray crystal structure analysis revealed that this compound is not *cis*-[$RuCl_2$(COD)(tmeda)], but in fact a complex resulting from the dealkylation of the chelating tmeda ligand, namely, *trans*-[$RuCl_2$(COD)-($Me_2NCH_2CH_2NHMe$)] (**2**) (Scheme 2).

Scheme 2. Unexpected Synthesis of 2



2

An ORTEP view of complex **2** is shown in Figure 1, together with the most relevant bond distances and angles.

The structure of **2** is distorted octahedral, with the two chloride atoms occupying mutually *trans*-positions, but with an angle Cl(1)−Ru(1)−Cl(2) of 161.96(2)° which deviates significantly from linearity. The midpoints of the double bonds of the COD ligand and the nitrogen atoms of the diamine ligand are in the equatorial positions. The overall structure is very similar in ligand arrangement and dimensions to that of the parent compound *trans*-[$RuCl_2$(COD)-(tmeda)],[17] but replacing one of the methyl groups in tmeda by one hydrogen atom. It also resembles the structure of *trans*-[$RuCl_2$(COD)($EtNHCH_2CH_2NHEt$)].[18] The most relevant feature of the structure of **2** is the fact that the Ru(1)−N(1) and Ru(1)−N(2) bond distances have significantly different values, 2.259(2) and 2.163(2) Å, respectively. This difference in the Ru−N separations involving secondary and tertiary nitrogen atoms has also been observed in the structure for the complex *trans*-[$RuCl_2$(NBD)($Et_2NCH_2CH_2NHEt$)].[15] In any case, all the bond lengths and angles are within expected ranges. We have reexamined the spectral data of **2** in the light of its true structure. The observed IR band at 3218 cm^{-1} is fully

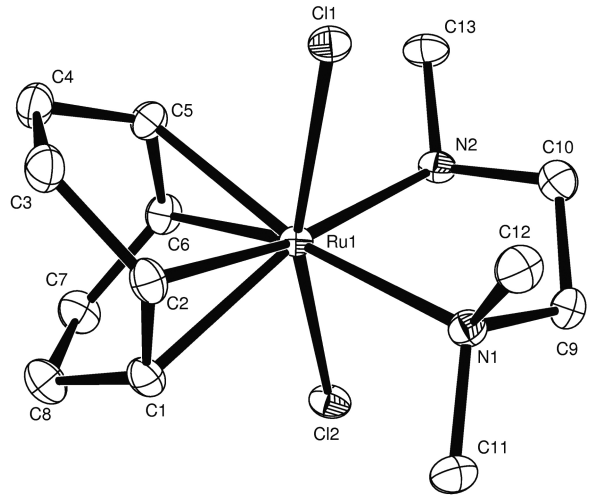


Figure 1. ORTEP drawing (50% displacement ellipsoids, hydrogen atoms omitted) of *trans*-[$RuCl_2$(COD)($Me_2NCH_2CH_2NHMe$)] (**2**). Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru(1)−Cl(1) 2.4227(7), Ru(1)−Cl(2) 2.4472(7), Ru(1)−N(1) 2.259(2), Ru(1)−N(2) 2.163(2), Ru(1)−C(1) 2.210(2), Ru(1)−C(2) 2.204(2), Ru(1)−C(5) 2.206(2), Ru(1)−C(6) 2.212(2), C(1)−C(2) 1.387(4), C(5)−C(6) 1.385(4); Cl(1)−Ru(1)−Cl(2) 161.96(2), N(1)−Ru(1)−N(2) 81.52(6), Cl(1)−Ru(1)−N(1) 86.21(5), Cl(1)−Ru(1)−N(2) 82.97(5), Cl(2)−Ru(1)−N(1) 83.86(5), Cl(2)−Ru(1)−N(2) 80.70(5), C(1)−Ru(1)−C(2) 36.62(8), C(5)−Ru(1)−C(6) 36.54(9).

consistent with the presence of the N−H bond. Because of the substitution of one methyl group by one hydrogen atom attached to nitrogen, the symmetry of the molecule is lost and all proton and carbon atoms become magnetically inequivalent. Thus, three resonances are observed for the methyl groups of the *N,N,N′*-trimethylethylenediamine ligand in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The resonance for the methyl group on the secondary nitrogen atom appears as one doublet in the ^1H NMR spectrum due to coupling with the NH proton, as inferred from a gCOSY 2D NMR experiment. The NH proton is not observed in CD_2Cl_2 solution due most likely to fast exchange, but appears as one broad singlet at 3.6 ppm if the spectrum is recorded in C_6D_6. It seems odd that this compound was previously mischaracterized as *cis*-[$RuCl_2$(COD)(tmeda)], given the fact that only three methyl resonances instead of four were reported to be present in its $^{13}C\{^1H\}$ NMR spectrum.[15] Although the presence of four methyl resonances in its ^1H NMR spectrum was reported, for **2** actually there are only three, one of them being a doublet signal (due to coupling with NH proton). Furthermore, the reported microanalysis figures calculated for the alleged *cis*-[$RuCl_2$(COD)(tmeda)] required the inclusion of half a molecule of water in order to account for the values found experimentally.[15] However, those microanalytical values of found C, H, and N content fit well with the composition of the actual compound **2**, as expected. Studies carried out on the catalytic hydrogenation of ketones using the compound claimed to be *cis*-[$RuCl_2$(COD)(tmeda)][15] need some revision in the light of new evidence, since the actual catalyst precursor used in such experiments was compound **2**.

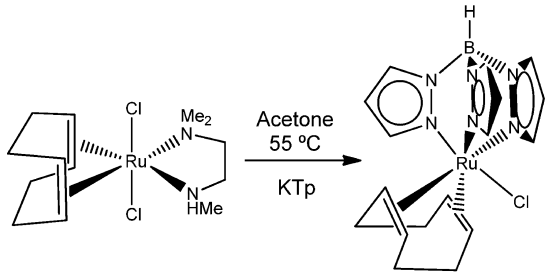
Compound **2** is, therefore, generated by dealkylation of the tmeda ligand, which is transformed into a trimethylethylenediamine ligand. Dealkylation processes involving chelating diamines with Ru^{II} complexes have been studied in detail, and it has been possible to establish that they are intramolecular

DOI: 10.1021/om501307a
Organometallics 2015, 34, 1001−1004

in nature.[15,18] The dealkylation of tmeda in *trans*-[$RuCl_2$(COD)(tmeda)] had been overlooked. Furthermore, it was remarked upon the fact that the loss of one or even two alkyl fragments takes place in complexes containing the more sterically demanding ligand *N,N,N′,N′*-tetraethylethylenediamine (teeda) but not with tmeda.[15] It becomes clear that the tmeda ligand in these complexes also undergoes a similar dealkylation process as their counterparts with teeda. These observations suggest that amine dealkylation processes might be more common and widespread than previously anticipated. An important difference between the metal-mediated dealkylation in tmeda and in teeda is that, in the latter, the formal loss of one ethylene molecule (C_2H_4) occurs, whereas in the case of tmeda, the loss corresponds to a "CH_2" moiety. The fate of this "CH_2" fragment is unknown at present. It might eventually undergo dimerization to yield ethylene, or it might be trapped by some of the molecules present in the reaction mixture.

As a conclusion, the search for an atom-economical synthetic procedure for the preparation of the versatile precursor **1** has revealed an overlooked dealkylation process involving *trans*-[$RuCl_2$(COD)(tmeda)] and leading to complex **2**. The reaction of **2** with KTp has shown to be an efficient method for the preparation of **1** (Scheme 3).

Scheme 3



2 **1**

The overall yield of **1** based upon the starting amount of [{$RuCl_2$(COD)}$_n$] is ca. 52%, a value that is slightly higher than the alternative procedure using [$RuCl_2$(COD)(MeCN)$_2$] (42–48% based upon the starting amount of [{$RuCl_2$(COD)}$_n$]).[8,13] Both synthetic procedures work far better in terms of atom economy and waste generation than the classic route involving the use of salts of the complex [$RuH(COD)(NH_2NMe_2)_3$]$^+$. Hence, the use of the methodology reported in the present work becomes one of the recommended alternatives for the synthesis of **1**.

EXPERIMENTAL SECTION

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40–60 °C) were obtained oxygen- and water-free from a solvent purification apparatus. Acetone, dichloromethane, and toluene were of anhydrous quality and used as received. All solvents were deoxygenated immediately before use. The grade of purity of tmeda was >99.5% (Aldrich, purified by redistillation). It was additionally purified by distillation over calcium hydride under argon. Polymeric [{$RuCl_2$(COD)}$_n$][19] and KTp[20] were prepared according to reported procedures. NMR spectra were taken on a spectrometer operating at 500 MHz (^{1}H frequency). Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and $^{13}C\{^1H\}$). ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic signal assignments were confirmed by ^{1}H-gCOSY and gHSQCAD (^{1}H–^{13}C) experiments. Microanalyses were performed at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

[$RuCl_2$(COD)($Me_2NCH_2CH_2NHMe$)] 2. To a slurry of [{$RuCl_2$(COD)}$_n$] (3.9 g, 13.9 mmol) in toluene (50 mL), an excess of tmeda (4.5 mL, ca. 30 mmol) was added via syringe. The mixture was heated at 80 °C for 72 h. The solvent was removed in vacuo, the residue was extracted with a mixture dichloromethane:diethyl ether 1:4, and the solution was filtered. Removal of the solvent in vacuo yielded a sticky yellow-brown solid, which was triturated with petroleum ether until a yellow precipitate was obtained. It was filtered, washed with petroleum ether, and dried in vacuo. This crude material always contains 20–25% of *trans*-[$RuCl_2$(COD)(tmeda)], but this does not represent an inconvenience to its use in the subsequent step, the reaction with KTp to yield **1**. Yellow-orange crystals of pure **2** were obtained by recrystallization of the crude material from dichloromethane/petroleum ether. Yield: 4.70 g, 86%. Anal. Calcd for $C_{13}H_{26}N_2Cl_2Ru$: C, 40.84; H, 6.85; N, 7.33. Found: C, 40.73; H, 6.88; N, 7.20. IR: ν(NH) 3218 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 4.28, 4.19, 4.08, 4.02 (m, 1 H each, =C*H* for COD), 3.37, 1.88 (m, 1 H each, $(CH_3)_2NCH_2$), 3.06, 2.62 (m, 1 H each, $(CH_3)HNCH_2$), 2.79 (m, 2 H, CH_2 for COD), 2.55, 2.46 (s, 3 H each, $(CH_3)_2NCH_2$), 2.28 (d, ^3J(H,H) = 6.4 Hz, 3 H, $(CH_3)HNCH_2$), 2.23 (m, 3 H, CH_2 for COD), 2.11, 1.65, 1.54 (m, 1 H each, CH_2 for COD); $^{13}C\{^1H\}$ NMR (125.67 MHz, CD_2Cl_2, 298 K): δ 89.5, 88.4, 87.3, 85.7 (s, =CH for COD), 61.5 (s, $(CH_3)_2NCH_2$), 52.5 (s, $(CH_3)HNCH_2$), 51.1, 50.7 (s, $(CH_3)_2N$), 36.4 (s, $(CH_3)HN$), 31.5, 31.1, 28.7, 28.1 (s, CH_2 for COD).

[TpRuCl(COD)] 1. To a mixture of [$RuCl_2$(COD)($Me_2NCH_2CH_2NHMe$)] (4.6 g, 12 mmol) and KTp (3.0 g, 12 mmol), acetone (30 mL) was added. The mixture was heated at 55 °C. Upon a few minutes stirring at this temperature, a yellow precipitate of **1** was formed. The mixture was stirred for 2 h at 55 °C. Then, the volume was reduced to approximately one-half, and the mixture cooled to −20 °C. The yellow precipitate was filtered off, washed with petroleum ether, and dried in vacuo. The crude product was dissolved in CH_2Cl_2, and the KCl was removed by filtration over Celite. Removal of the solvent from the filtered solution in vacuo afforded analytically pure **1**. Yield: 3.2 g, 60%. Anal. Calcd for $C_{17}H_{22}N_6BClRu$: C, 44.61; H, 4.84; N, 18.36. Found: C, 44.58; H, 4.95; N, 18.21. IR: ν(BH) 2502 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.13 (d, 1 H), 7.79 (d, 1 H), 7.65 (d, 2 H), 7.57 (d, 2 H), 6.32 (t, 1 H), 6.21 (t, 2 H) ($HB(C_3H_3N_2)_3$), 4.91, 4.03 (m, 2 H each, =C*H* for COD), 2.95, 2.69, 2.42, 2.26 (m, 2 H each, CH_2 for COD); $^{13}C\{^1H\}$ NMR (125.67 MHz, $CDCl_3$, 298 K): δ 145.0, 141.7, 137.5, 134.8, 106.2, 106.1 (s, $HB(C_3H_3N_3)_3$), 94.5, 87.0 (s, =CH for COD), 30.4, 29.7 (s, CH_2 for COD).

X-ray Structure Determination. Crystals of **2** were obtained by recrystallization from dichloromethane/petroleum ether. X-ray diffraction data were collected at 100 K on a 3-circle diffractometer with a CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using Mo Kα radiation (λ = 0.71073 Å). Four sets of frames were recorded over a hemisphere of the reciprocal space by ω scans with $\delta(\omega)$ = 0.30 and an exposure of 10 s per frame. No significant decay was observed over the course of data collection. Intensity data were corrected for Lorentz and polarization effects and absorption corrections applied using SADABS.[21] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELX97)[22] by using all unique data. All non-hydrogen atoms were refined anisotropically with hydrogen atoms included in calculated positions (riding model). The program ORTEP-3[23] was used for plotting. In the Supporting Information, Table S1 summarizes the crystal data and data collection and refinement details for **2**.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format for compound **2**. Crystal data and experimental details for the crystal structure determination (Table S1). ^{1}H and $^{13}C\{^1H\}$ NMR spectra of

DOI: 10.1021/om501307a
Organometallics 2015, 34, 1001–1004

2 (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org. The crystal structure of **2** has been also deposited at Cambridge Crystallographic Data System with reference CCDC 1006450.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: manuel.tenorio@uca.es (M.J.-T.).
*E-mail: carmen.puerta@uca.es (M.C.P.).

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

We thank Prof. Pedro J. Pérez (Universidad de Huelva, Spain) and Prof. M. C. Nicasio (Universidad de Sevilla, Spain) for the valuable suggestions and constructive criticism made upon reading the manuscript. We also wish to thank the Spanish Ministerio de Economia y Competitividad (Project CTQ2010-15390) and Junta de Andalucía (PAIDI FQM188) for financial support.

REFERENCES

(1) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998−4004.
(2) Pavlik, S.; Gemel, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Organomet. Chem.* **2001**, *617*−*618*, 301−310.
(3) Standfest-Hauser, C.; Mereiter, C.; Schmid, R.; Kirchner, K. *Organometallics* **2004**, *23*, 2194−2196.
(4) Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. *Organometallics* **2005**, *24*, 3561−3575.
(5) Pavlik, S.; Puchberger, M.; Mereiter, K.; Kirchner, K. *Eur. J. Inorg. Chem.* **2006**, 4137−4142.
(6) Becker, E.; Pavlik, S.; Kirchner, K. *Adv. Organomet. Chem.* **2008**, *56*, 155−197.
(7) Fernández, F.; Puerta, M. C.; Valerga, P. *Inorg. Chem.* **2013**, *52*, 4396−4410.
(8) Ali, A.; Malan, F. P.; Singleton, E.; Meijboom, R. *Organometallics* **2014**, *33*, 5983−5989.
(9) Ashwort, T. V.; Singleton, E.; Hough, J. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1809−1815.
(10) Albers, M. O.; Crosby, S. F. A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2014−2017.
(11) Jalón, F.; Otero, A.; Rodríguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1629−1633.
(12) Ashworth, T. V.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Coville, N. J.; Darling, E.; Markwell, A. J. *S. Afr. J. Chem.* **1987**, *40*, 183−188.
(13) Wilson, D. C.; Nelson, J. H. *J. Organomet. Chem.* **2003**, *682*, 272−289.
(14) Gómez, J.; Gemel, C.; Slugovc, C.; Wozniak, E.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **2001**, *132*, 1137−1143.
(15) Morilla, M. E.; Rodríguez, P.; Belderraín, T.; Graiff, C.; Tiripicchio, A.; Nicasio, M. C.; Pérez, P. J. *Inorg. Chem.* **2007**, *46*, 9405−9414.
(16) (a) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132−3139. (b) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278−6288.
(17) Harvey, B. G.; Shi, Y.; Peterson, B. K.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **2006**, *359*, 839−845.
(18) Morilla, M. E.; Morfes, G.; Nicasio, M. C.; Belderraín, T.; Díaz-Requejo, M. M.; Graiff, C.; Tiripicchio, A.; Sánchez-Delgado, R.; Pérez, P. J. *Chem. Commun.* **2002**, 1848−1849.
(19) Abel, E. W.; Bennet, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178−3182.
(20) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99−109.
(21) Sheldrick, G. M. *SADABS, 2001 version*; University of Göttingen: Göttingen, Germany, 2001.
(22) (a) Sheldrick, G. M. *SHELXTL version 6.10: Crystal Structure Analysis Package*; Bruker AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.
(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

DOI: 10.1021/om501307a
Organometallics 2015, 34, 1001−1004