DOI: 10.1002/ejic.200600320

DFT-Verified Crystallographic Mechanism of Cycloplatination

Stefanus Otto,*[a][‡] Arani Chanda,[b] Pavel V. Samuleev,[c] and Alexander D. Ryabov*[b]

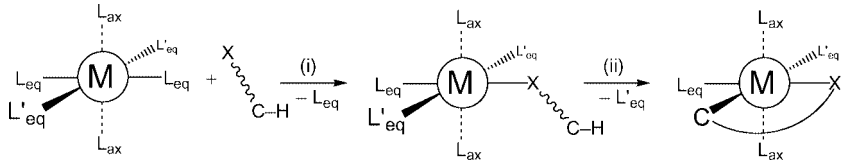
Keywords: Platinum / C-H activation / Metallacycles / X-ray diffraction / Density functional calculations

Two key intermediates in the mechanistic cycle of cycloplatination of aryl oximes by Pt^{II} complexes were crystallographically characterized. *trans*-[$PtCl_2(SOMe_2)$(*N*-acetophenone oxime)] is an active precursor on the C–H cleavage reaction coordinate. The formation of *trans*-[$PtCl_2$(*N*-benzaldehyde oxime)$_2$] accounts for the rate retardation by excess oxime. DFT calculations support the crystallographic evidence that provides unequivocal proof for the electrophilic nature of cycloplatination.

Disclosure of mechanisms of cyclometalation by transition-metal complexes is a difficult task.[1a] Cyclometalation is a multistep event that should include (i) ligand coordination to a metal center through its usually N, P, O, or S donor site (X), and (ii) a stepwise metal-involved cleavage of the C–H bond (Scheme 1).

Step (i) is an intermolecular ligand substitution, which may occur through associative, dissociative, or interchange pathways. Step (ii) is a combination of intramolecular ligand substitution and C–H cleavage. Options for the C–H cleavage include oxidative addition/reductive elimination, electrophilic substitution, or multicentered activation (σ-bond metathesis).[1a,1b] Agostic interactions[2] are also often included in a mechanistic picture.[3] Consequently, extensive efforts are required for the unequivocal understanding of cyclometalation mechanisms. A complicating factor is that mechanistic studies are often performed with excess incoming ligand X~C–H and may result in the binding of more than one ligand to the metal center.

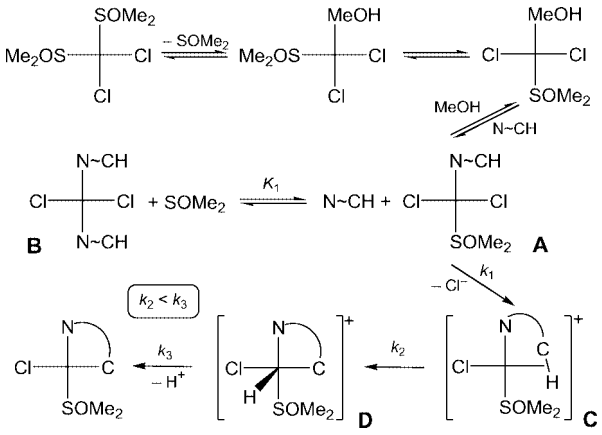
All stated above apply to cycloplatination by the Pt^{II} sulfide and sulfoxide complexes [$PtCl_2(SR_2)_2$] or [$PtCl_2(SOR_2)_2$]. These metalating agents are very convenient for performing various cycloplatination reactions,[4] and the use of chiral sulfoxides SORR′ allows for the synthesis of platinacycles with the planar[5a] and central carbon chirality.[5b] We recently reported on the mechanism of cycloplatination of aryl oximes by [$PtCl_2(SR_2)_2$] or *cis*-[$PtCl_2(SOR_2)_2$] (R = Me) as shown in Scheme 2.[6] Evidence was presented that the cycloplatination is a multistep process and the principal reaction steps were recognized. The key intermediate was identified as complex **A**, which supports the views of other authors.[7] The formation of dichlorobis(*N*-oxime)platinum(II) **B** was postulated to account for the rate retardation by excess acetophenone oxime. Our deductions were based on kinetic and ^{1}H NMR spectroscopic data that may leave room for alternative interpretations. In this communication, we report X-ray crystallographic data for the compounds matching the intermediates **A** and **B**. They are complexes **1** and **2**, respectively. Although mechanistic chemists should apply caution when using solid-state information for the interpretation of kinetic data obtained in solution, the structures of complexes **A** and **B** are exceptionally mechanistically informative towards the dynamics of intramolecular C–H bond activation by Pt^{II}. The mech-



Scheme 1. General scheme for cyclometalation by octahedral or square-planar (L_{ax} = 0) transition metal complexes. Here L_{eq} and L_{ax} are equatorial and axial ligands, respectively.

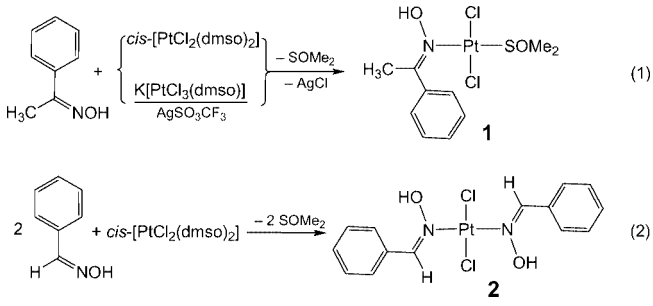
[a] Department of Chemistry, University of the Free State, P. O. Box 339, Bloemfontein 9300, South Africa
[b] Department of Chemistry, Carnegie Mellon University, 4400 Fifth Av., Pittsburgh, PA 15213, USA
E-mail: ryabov@andrew.cmu.edu
[c] Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russia
[‡] Current address: Sasol Technology R & D, P. O. Box 1, Sasolburg 1947, South Africa, E-mail: Fanie.Otto@sasol.com
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

anistic conclusions made were verified, supported, and refined by theoretical analysis of key participants in Scheme 2 with DFT calculations.



Scheme 2. Mechanism of cycloplatination of aryl oximes by *cis*-$[PtCl_2(dmso)_2]$ suggested in ref.[6]

Compounds **1** and **2** were synthesized according to Equations (1) and (2), respectively, and characterized by ^1H NMR spectroscopy, analytical data, and X-ray crystallography. Crystal structures of **1** and **2** are displayed in Figure 1. Both complexes exhibit a square-planar geometry. The N-atom of the acetophenone oxime is in *trans* position relative to the sulfur atom of dmso in complex **1**. The phenyl plane of the oxime ligand is orientated almost perpendicularly to the metal plane with a Cl(1)–Pt–N–C(10) torsion angle of 69.1°. The phenyl ring is in the axial position with a closest Pt···C(16) contact of 3.153 Å [Pt···H(16) 2.852 Å]. The Pt–S(1) and Pt–N(1) bond lengths of 2.206(3) and 2.051(9) Å, respectively, are within normal ranges for bonds of this type. The Pt–Cl(1) and Pt–Cl(2) bond lengths of 2.287(3) and 2.293(3) Å, respectively, do not differ significantly and are within expected ranges.



Compound **2** crystallizes with the inversion center in the triclinic space group $P\bar{1}$ resulting in a mutually *trans* configuration of the oxime and chloro ligands with the oxime ligands located in the coordination plane. The hydroxy group is directed towards a chloro ligand, typical of many oxime complexes of Pd and Pt.[8] There is a Cl···H–O interaction, with Cl···O and Cl···H separations of 3.056 and 2.408 Å, respectively. The Pt–Cl(1) and Pt–N(1) bond lengths of 2.3053(19) and 2.021(6) Å, respectively, are within normal ranges for complexes of this type.

Crystallographically characterized species **1** and **2** do prove unambiguously the existence of the proposed intermediates **A** and **B**, respectively, shown in Scheme 2. Importantly, both structural and DFT (see below) data provide evidence why complex **B** is not on the reaction coordinate. In contrast, **A** is adequately pre-organized for subsequent metalation of the C–H bond. The azomethine unit geometry is an essential feature. Data in Figure 1 confirm the (*E*) and (*Z*) configuration of the C=N unit in complexes **1** and **2**, respectively. To avoid any confusion, all assignments are made for imaginary free aryl oximes, which are *not* bound to Pt^{II}. The (*Z*) geometry in **2** implies that the *trans*-bis(oxime)platinum(II) unit should be unreactive towards cyclometalation. The *ortho* C–H bonds are located too far from the metal center with a shortest Pt···H–C(16) distance of 4.916 Å. In contrast to **2**, the geometry at the C=N unit in

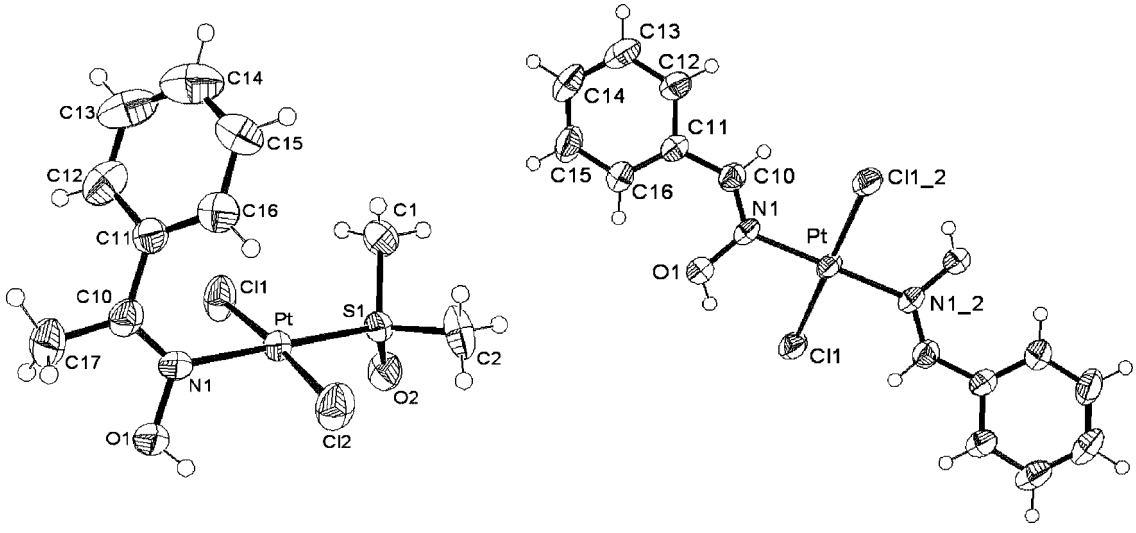


Figure 1. ORTEP diagrams of **1** (left) and **2** (right) at 30% probability level. Hydrogen atoms are of arbitrary size. Selected bond lengths [Å]: **1**: Pt–Cl(1) 2.287(3), Pt–Cl(2) 2.293(3), Pt–N(1) 2.051(9), Pt–S(1) 2.206(3); **2**: Pt–Cl(1) 2.3053(19), Pt–N(1) 2.021(6).

the mono(aryl oxime) complex **1** is (*E*) resulting in **1** being much better arranged for the subsequent C–H bond activation. In fact, different geometries at the C=N moiety in monomeric bis- and mono(oxime) complexes of Pt^{II} is a notable observation because the aspect of geometric isomerization at the C=N bonds was rather confusing. This is understandable because the geometry of ligands in free and cyclometalated states may be different. For example, azomethines are sometime involved in (*E*) → (*Z*) isomerization during cyclometalation.[4j] As in the case of **1**, the binding of the (*E*) form of the aryl oxime delivers its *ortho* C–H bond to the proximity of the metal center. The Pt···C(16) separation is only 3.153 Å. For comparison, Pt^{II} is further away from the C–H bond of the Cp ring in *trans*-[$PtCl_2(CpFeC_5H_4CMe{=}NPh)$dmso] and therefore an additional external base is needed to facilitate the C–H bond cleavage.[9] Note that cycloplatination of **1** occurs spontaneously in methanol without basic co-catalyst.

Assuming that the short Pt···C(16) separation is evidence that complex **1** is on the reaction coordinate, several comments could be made based on mutual atom arrangement in **1**. The C(16) atom is located right above the Pt–N bond and H(16) is directed at Cl(2). Therefore, there is a favorable setup of all key groups involved in cycloplatination for an easy conversion of **A** into **C** (Scheme 2). Essential is just the dissociation of chloride Cl(2) that gives intermediate **C**. Based on the data reported here, elsewhere,[6,10,11] and the results of DFT analysis of this particular system (see below) we suggest a first DFT-verified "crystallographic" mechanism of cycloplatination by *cis*-[$PtCl_2(SOMe_2)_2$] (Figure 2), which actually involves all major steps of the "kinetic" mechanism in Scheme 2. A strength of the "crystallographic" mechanism is that ***all*** the compounds in Figure 2 have now been characterized by X-ray crystallography including the starting complex *cis*-[$PtCl_2(SOMe_2)_2$] and the incoming aryl oxime.

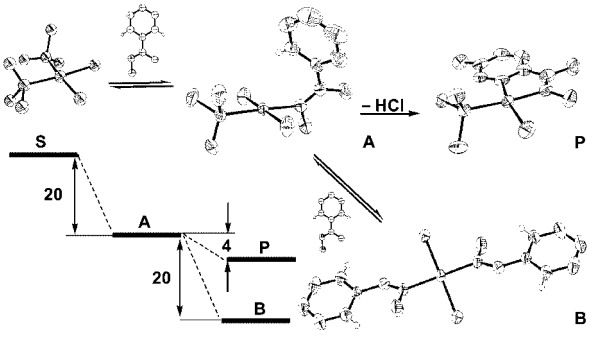


Figure 2. "Crystallographic" mechanism of cycloplatination of aryl oximes by *cis*-[$PtCl_2(SOMe_2)_2$]. X-ray data for Pt^{II} complexes **S** and **P** are from ref.[10] and ref.[6], respectively; structures **A** and **B** are reported in this work. A structure of (*E*)-acetophenone oxime was published by Gieren, et al.[11] At the bottom left is the DFT-calculated diagram with energies in kcal mol^{-1}.

The geometries of all structures in Figure 2 are optimized using Becke's three-parameter hybrid potential (B3LYP) with LANL2DZ basis set as provided by Gaussian 03.[12] Optimizations are done in the absence of any solvent. The optimized geometries are in general agreement with the experimental bond lengths/angles. Longer Pt–Cl and Pt–S but shorter Cl···HO bond lengths (all by 0.1–0.2 Å) were, however, observed. Substitution of the S- by the N-donor ligand to form intermediate **A** is energetically favorable (ca. 20 kcal mol^{-1}), as well as the second exergonic substitution leading to **B**. As a result, *Z* configured intermediate **B** is in a deep energy well and its C–H bonds are inaccessible for cycloplatination (Figure 2).

Our theoretical simulations indicate that the C–H bond activation (**A** → **P**) ***never*** occurs when both chloride ions are bound to Pt^{II}. In other words, there is no C–H breaking pathway through an axial agostic contact. The evidence for the C–H bond activation begins to emerge after enforced dissociation of chloride as shown in Figure 3. Here, complex **A′** is generated by removing one chloride ion from the DFT-optimized structure of **A**. Geometry optimization of **A′** results in **C′**, which matches nicely the postulated intermediate **C** in Scheme 2. Remarkably, the C–H bond carbon atom in **C′** aligns itself *in the metal plane* and is almost ideally *trans* to the chloro ligand with a C···Pt–Cl angle of 165°. Hence, the in-plane disposition of the C–H bond is absolutely crucial for the reaction to happen. The Pt–C distance changes from 3.153 Å (in **A**) to 2.519 Å in **C′** to become finally 2.021 Å in **P**. The Mulliken charge on the carbon atom varies drastically as well, viz. –0.304 (**A**) → –0.449 (**C′**) → –0.193 (**P**), indicating a major development of a carbanion character of the C–H bond carbon atom in high-energy intermediate **C′**. Elongation of the C^1–C^2 bond (1.438 vs. average 1.410 Å for other aryl C–C bonds of **C′**, Figure 3) supports also the "carbanionic" hypothesis. This also shows that the hydrogen atom should dissociate rather as proton in an electrophilic substitution sequence. DFT calculations show that the cycloplatination of the C–H bond (**A** → **P**) is 4–5 kcal mol^{-1} favorable when the leaving HCl is allowed to interact with product **P**.[13] If the energies of **P** and HCl are calculated separately, the cycloplatination reaction is ca. 10 kcal mol^{-1} endergonic. This scenario may be different in the presence of methanol as solvent where H-bonding should play a significant role. Apparently, the chloro ligand is somehow involved in the stabilization of the leaving hydrogen atom. Mechanistic options are either chloride interacts with H^+ as a base, thus precluding reverse

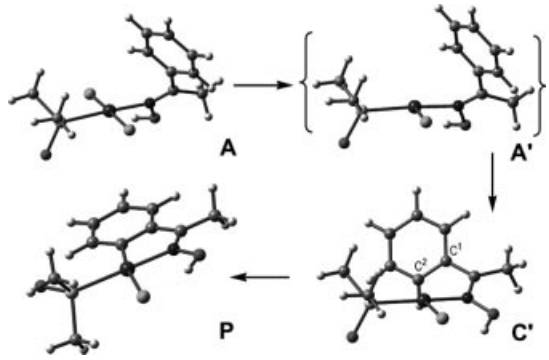


Figure 3. DFT-optimized structures of intermediates **A**, **C′**, and product **P**, see text for details.

protonolysis of the Pt–C bond of **P**, or its role is a compensation of a positive charge of intermediate **D** in Scheme 2.

In conclusion, a combination of kinetic and X-ray structural data plus theoretical DFT information generated a unified, self-consistent detailed mechanistic picture of the electrophilic C–H bond cyclometalation by platinum(II). The DFT routine filled elegantly the mechanistic gaps, about which kinetics and crystallography are usually silent.

Experimental Section

Chemicals: Acetophenone oxime (Acros), benzaldehyde oxime (Acros), $SOMe_2$ (Merck) and $AgSO_3CF_3$ (Aldrich) were used as received, methanol (Riedel–de Haën) was of analytical grade and was freshly distilled from CaH_2 under dinitrogen prior to use.

NMR Measurements: The ^1H NMR spectra were recorded at 295 K as CD_3OD or $CDCl_3$ solutions with either a Bruker 300 MHz or a Varian Unity 300 spectrometer operating at 299.78 MHz; the spectra were calibrated relative to TMS at $\delta = 0$ ppm.

Preparation of Complexes: $K[PtCl_3(SOMe_2)]$ and *cis*-$[PtCl_2(SOMe_2)_2]$ were prepared according to literature procedures.[14,15]

***trans*-[PtCl$_2${HO–N=C(CH$_3$)C$_6$H$_5$}(SOMe$_2$)] (1). (a)** A homogeneous solution of *cis*-$[PtCl_2(SOMe_2)_2]$ (104 mg, 0.246 mmol) was prepared in methanol (30 mL) by gently heating with effective stirring for 2 h. Acetophenone oxime (35 mg, 0.26 mmol) in methanol (5 mL) was added at ambient temperature and the solution was stirred for 30 min. The reaction mixture was concentrated to 20 mL under a flow of nitrogen and left at 15 °C to crystallize by slow evaporation of methanol. Crystals of **1** suitable for X-ray diffraction were obtained. **(b)** $AgSO_3CF_3$ (64 mg, 0.25 mmol), dissolved in methanol (5 mL), was added to a solution of $K[PtCl_3(SOMe_2)]$ (100 mg, 0.239 mmol), also in methanol (25 mL). The resulting mixture was stirred for 15 min to facilitate the precipitation of AgCl and was subsequently filtered to yield a clear solution. Acetophenone oxime (34 mg, 0.25 mmol) in methanol (5 mL) was added at ambient temperature and the solution was stirred for 10 min. Evaporation of the methanol resulted in isolation of **1** in almost quantitative yield. ^1H NMR ($CDCl_3$): δ = 2.50 (s, 3 H, CCH_3), 3.24 (t, $^3J_{PtH}$ 19 Hz, 6 H, SCH_3), 7.50 (m, 3 H, 2-H, 4-H, 6-H), 7.90 (m, 2 H, 3-H, 5-H), 8.00 (s, 1 H, OH) ppm. $C_{10}H_{15}Cl_2NO_2PtS$ (477.98): calcd. C 25.1, H 3.2, N 2.9; found C 25.4, H 3.6, N 2.7.

***trans*-[PtCl$_2$(HO–N=CHC$_6$H$_5$)$_2$] (2):** Benzaldehyde oxime (592 mg, 4.89 mmol) was added to a solution of $K[PtCl_3(SOMe_2)]$ (210 mg, 0.50 mmol) in methanol (25 mL) and the reaction mixture was subsequently refluxed for 4 d. The reaction progress was monitored by ^1H NMR spectroscopy as described previously.[6] Yield 119 mg (48%). ^1H NMR ($CDCl_3$): δ = 7.4–7.6 (m, 6 H, 2× 2-H, 2× 4-H, 2× 6-H), 7.93 (m, 4 H, 2× 3-H, 2× 5-H), 8.19 (t, $^3J_{PtH}$ = 22 Hz, 2 H, 2× CH), 9.56 (s, 2 H, 2× OH) ppm. $C_{14}H_{14}Cl_2N_2O_2Pt$ (507.01): calcd. C 33.1, H 2.8, N 5.5; found C 33.4, H 3.0, N 5.4.

Crystallography: The data collections were carried out with a Siemens SMART CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) and ω-scans at 293(2) K. After completion of the data collection, the first 50 frames were repeated to check for decay, of which none was observed. All reflections were merged and integrated using SAINT[16] and were corrected for Lorentz, polarization and absorption effects using SADABS.[17] The structure was solved by the heavy-atom method and refined through full-matrix least-squares cycles using the SHELXL97[18] software package with $\Sigma(|F_o| - |F_c|)^2$ being minimized. All non-H atoms were refined with anisotropic displacement parameters while the H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms (aromatic C–H 0.93 Å, aliphatic C–H 0.96 Å, O–H 0.82 Å). For both structures the minimum and maximum residual electron densities were located within 1 Å of the platinum nuclei indicating no physical meaning. The crystal data and details of the data collection and refinement are given in Table S1 with selected geometrical parameters in Table S2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC-290273 and -290274 (**2** and **1**, respectively). 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): Crystal data and structure refinement parameters, bond lengths and bond angles in Tables S1 and S2.

Acknowledgments

The University of Lund, Sweden, is thanked for the use of their diffractometer. The University of the Free State is acknowledged for financial support.

[1] a) A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403; b) M. Lersch, M. Tilset, *Chem. Rev.* **2005**, *105*, 2471.
[2] M. Brookhart, M. L. H. Green, L. L. Wong, *Progr. Inorg. Chem.* **1988**, *36*, 1.
[3] See for example: a) P. S. Pregosin, F. Wombacher, *Magn. Reson. Chem.* **1991**, *29*, S106; b) A. Albinati, F. Lianza, B. Muller, P. S. Pregosin, *Inorg. Chim. Acta* **1993**, *208*, 119; c) M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398; d) R. Romeo, M. R. Plutino, A. Romeo, *Helv. Chim. Acta* **2005**, *88*, 507; e) R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083; f) D. L. Davies, S. M. A. Donald, S. A. Macgregor, *J. Am. Chem. Soc.* **2005**, *127*, 13754.
[4] a) P. R. R. Ranatunge-Bandarage, B. H. Robinson, J. Simpson, *Organometallics* **1994**, *13*, 500; b) Y. J. Wu, Y. H. Liu, X. L. Cui, H. Z. Yuan, X. A. Mao, *Polyhedron* **1996**, *15*, 3315; c) A. D. Ryabov, G. M. Kazankov, I. M. Panyashkina, O. V. Grozovsky, O. G. Dyachenko, V. A. Polyakov, L. G. Kuz'mina, *J. Chem. Soc., Dalton Trans.* **1997**, 4385; d) L. Ding, D. P. Zou, Y. J. Wu, *Polyhedron* **1998**, *17*, 2511; e) M. D. Meijer, A. W. Kleij, M. Lutz, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **2001**, *640*, 166; f) M. D. Meijer, E. de Wolf, M. A. L. Lutz, G. Spek, P. M. van Klink, G. van Koten, *Organometallics* **2001**, *20*, 4198; g) M. D. Meijer, A. W. Kleij, B. S. Williams, D. Ellis, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2002**, *21*, 264; h) S. Perez, C. Lopez, A. Caubet, X. Solans, M. Font-Bardia, *New J. Chem.* **2003**, *27*, 975–982; i) A. Caubet, C. Lopez, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* **2003**, *669*, 164; j) M. Crespo, M. Font-Bardia, J. Granell, M. Martinez, X. Solans, *Dalton Trans.* **2003**, 3763; k) C. Lopez, A. Caubet, S. Perez, X. Solans, M. Font-Bardia, *Chem. Commun.* **2004**, 540.
[5] a) A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov, J. A. K. Howard, L. G. Kuz'mina, M. S. Datt, C. Sacht, *Organometallics* **1998**, *17*, 3615; b) A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov, A. Fischer, *Organometallics* **2002**, *21*, 1633.
[6] A. D. Ryabov, S. Otto, P. V. Samuleev, V. A. Polyakov, L. Alexandrova, G. M. Kazankov, S. Shova, M. Revenco, J. Lipkowski, M. H. Johansson, *Inorg. Chem.* **2002**, *41*, 4286.
[7] Y. Wu, S. Huo, J. Gong, X. Cui, L. Ding, K. Ding, C. Du, Y. Liu, M. Song, *J. Organomet. Chem.* **2001**, *637–639*, 27.
[8] a) A. D. Ryabov, G. M. Kazankov, A. K. Yatsimirsky, L. G. Kuz'mina, O. Y. Burtseva, N. V. Dvortsova, V. A. Polyakov, *In-*

org. Chem. **1992**, *31*, 3083; b) A. D. Ryabov, L. G. Kuz'mina, V. A. Polyakov, G. M. Kazankov, E. S. Ryabova, M. Pfeffer, R. van Eldik, *J. Chem. Soc., Dalton Trans.* **1995**, 999.
[9] Y. J. Wu, L. Ding, H. X. Wang, Y. H. Liu, H. Z. Yuan, X. A. Mao, *J. Organomet. Chem.* **1997**, *535*, 49.
[10] R. Melanson, F. D. Rochon, *Can. J. Chem.* **1975**, *53*, 2371–2374.
[11] A. Gieren, T. Huebner, C. Ruiz-Perez, *Chem.-Ztg.* **1986**, *110*, 73–76.
[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, release B.05, Wallingford, CT, USA, **2004**.
[13] In the optimised structure, HCl is H-bonded to the oxygen atom of coordinated dimethyl sulfoxide.
[14] V. Y. Kukushkin, A. J. L. Pombeiro, C. M. P. Ferreira, L.-I. Elding, *Inorg. Synth.* **2002**, *33*, 189–196.
[15] J. H. Price, A. N. Williamson, R. F. Schramm, B. B. Wayland, *Inorg. Chem.* **1972**, *11*, 1280.
[16] SAINT: *Siemens Analytical X-ray Instruments Inc*., Madison, Wisconsin, USA, **1995**.
[17] G. M. Sheldrick, University of Göttingen, Göttingen, Germany, **1996**.
[18] G. M. Sheldrick, *SHELXL97*, University of Göttingen, Göttingen, **1997**.

Received: March 21, 2006
Published Online: May 17, 2006

