High-valent Molybdenum Imido Complexes with Tethered Olefins

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Dedicated to Professor Hansgeorg Schnöckel on the Occasion of his 65th Birthday

Abstract. Against the background of the (propene)Mo(=O)(=NH) and (allyl)Mo(=O)(=NH) surface species suggested as intermediates of the SOHIO process the potential of $H_2N-C_6H_4-CH_2-CH=CH-CH_3$, (I), for the introduction of chelating imido/olefin or imido/allyl ligands at highvalent Mo centres was tested. Reaction of I with Na₂[MoO₄] and trimethylchlorosilane yielded [Cl₂Mo(=N-C₆H₄-CH₂-CH=CH-CH₃)₂(dme)] (1), containing pendant olefinic arms. All attempts to introduce the olefin into the coordination sphere of the Mo centre failed. The same observation was made with [Cl₂Mo(=O)(=N-C₆H₄-CH₂-CH= CH-CH₃)(dme)] (2), synthesised via a commutation reaction from 1 and[(dme)Cl₂Mo(=O)₂]. Reaction of three equivalents of I with [CpMoCl_{4'}] yields [CpCl₂Mo(= $N-C_6H_4-CH_2-CH=CH-CH_3$)], (3), again with a pendant olefin arm; the products of experiments aiming at coordinating it to the Mo atom eluded isolation. I thus does not seem suitable for the synthesis of complexes with imido/ olefin or imido/allyl ligands. However, products 1–3, (two of which (1, 3) were also characterised by single crystal X-ray diffraction) are nevertheless interesting, e.g., with respect to the grafting of molybdenum complexes on the surfaces of solid supports to obtain heterogeneous oxidation catalysts.

Keywords: Molybdenum; Imido complexes; Crystal structures; Olefin tether; SOHIO process

beside each other it would be interesting to investigate the

synthesis of complexes containing O=Mo=NR units that

are capable of binding olefin or allyl ligands. As the oxo

ligand therein makes the metal centre "harder" in compari-

son to a situation where the first imido ligand is joined by

a Cp ligand or a second imido ligand (vide supra), it should

be more difficult to coordinate the "soft" organic ligands.

Recently, we succeeded in synthesizing an allylmolyb-

denum(IV) complex (a very rare example of a π -allyl-Mo

complex where the metal centre is in a comparatively high

oxidation state and additionally binds hard chloro ligands)

via tethering of the allyl ligand to a coordinating donor

function [5]. Hence, the question arose whether allyl and/or

olefin ligands could be stabilized in the coordination sphere

of oxo/imido molybdenum complex metal fragments, when

these organic functions are tethered to the imido ligand.

First of all it had to be decided concerning the length of the tether between the potential imido ligand and the olefinic function (being substituted by an additional methyl group to grant the possibility of a later conversion to an allylic

unit). As in the previous work [5] it had proved reasonable

to integrate an arylic unit into the tether to establish at least

some rigidity, and as moreover Mo=N-Ar complexes are

a well studied class of compounds [6] we came down to a

decision between the ligands A and B (Chart 1).

Here we described the results obtained in that context.

Results and Discussion

Introduction

The acrylonitrile synthesis via propene oxidation in the presence of ammonia on bismuthmolybdate catalysts (SOHIO process) [1] is proposed to proceed via surface intermediates with π -olefin and π -allyl ligands bound to high-valent Mo^{V/VI} oxo/imido moieties [2]. These intermediates are considered to be very short-lived, as the combination of a "soft" π -olefin or π -allyl ligand with a "hard" molybdenum oxo/imido unit is naturally unstable, and, moreover, metal atoms in high oxidation states are not capable of stabilizing metal-ligand π -bonds by efficient backbonding.

This conception stimulates research with the aim of preparing molecular compounds that are modelled on this situation to see how these behave. *Green* et al. were able to prepare a [CpMo^{IV}(=NR)(π -allyl)] complex [3]. *Sundermeyer* et al. reported the synthesis of the compound [(t-BuN=)₂Mo^{VI}(allyl)₂], which could not be characterized structurally, but spectroscopic investigations hinted to a π coordination of one of the allyl ligands [4]. Since the bismuthmolybdate surface during the SOHIO process is suggested to contain both oxo and imido ligands at Mo^{VI} sites

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Chart 1 Potentially chelating imido/olefin ligands.

The results of DFT modelling studies for several situations gave rise to a choice in favour of **A**. Usually imido ligands are prepared starting form the corresponding amines which are reacted with Mo=O precursors under formal elimination of water. Accordingly, 2-(ⁿbut-2-en-1-yl)aniline (**I**), was synthesized starting from aniline and 3-chloro-1-butene which in the presence of Na₂CO₃ react at 100 °C to give a mixture of two different amines (Eq. (1)); subsequent treatment with sulfuric acid and work up yields pure **I** in form of a trans/cis mixture (7.2 : 1) [7].



As cis/trans isomerizations can be expected to occur in the presence of a metal centre anyway [5], the mixture was employed as such for subsequent reactions.

We started our investigation with diimido complexes whose synthesis is more facile than the one of oxo/imido complexes and which were envisioned to provide preliminary information concerning the potential of the strategy and the properties of ligand **A**. In analogy to the synthesis of molybdenumdiimido complexes reported previously by *Schrock* et al. [8] Na₂[MoO₄] was reacted with **I** and trimethylchlorosilane to give [Cl₂Mo(= $N-C_6H_4-CH_2-CH=CH-CH_3)_2(dme)$] (1) in 83 % yield after work up (Eq. (2)).

Starting from an isomeric mixture of I of course the formation of three stereoisomers of 1 could be expected; according to ¹H NMR spectroscopic investigations the trans : cis ratio for the ligands altogether amounted to 5.3 : 1, but it was not possible to determine the ratio of the individual stereoisomers of 1. Overlayering a solution of 1 in dichloromethane with pentane at -30 °C led to disordered crystals that were suitable for a rough crystal X-ray analysis. The result is shown in Figure 1, which illustrates one compound of the superposition structure. The ligands A display an all trans configuration.



Figure 1 Molecular structure of complex 1. All hydrogen atoms were omitted for clarity. Selected bond distances /Å and angles /°: Mo-N = 1.74 (2), Mo-Cl1 = 2.41 (1), Mo-Cl2 = 2.41 (1), N-C5 = 1.36(2), Mo-N-C5 = 167 (2).

The arrangement of the ligands around the metal atom can be described as distorted octahedral. The $Mo-N-C_{ar}$ units are almost linear (167°) which points to a singnificant $Mo\equiv N$ triple bond character. Accordingly, the average Mo-N bond distance is with 1.74 Å similar to comparable imido complexes containing a $Mo\equiv N$ triple bond [9].

In order to introduce the olefinic units of the pendant arms into the coordination sphere of the Mo atoms several experiments were performed. First of all it seemed desirable to replace the chloride by methyl ligands [10], as a subsequent treatment with $B(C_6F_5)_3$ would then lead to a cationic complex [11], where the olefinic function would find sufficient room at the metal atoms to coordinate (Eq. (3)).

Surprisingly, 1 behaved inert in the presence of two equivalents of MeMgI, while four equivalents led to a slow reduction. 1 was thus reacted directly with excessive $B(C_6F_5)_3$ and after work up the product was investigated NMR spectroscopically. The signals belonging to the dimethoxyethane ligand had vanished (probably due to acid/base reaction with the borane and precipitation), and there was only one set of signals for the ligand **A**. However, comparison of the chemical shifts with those of other d⁰-transition metal π -olefin complexes did not hint to a coordination of the olefinic units to the metal atom [12].



Despite this discouraging result we envisionened the syntheses of a mixed oxo/imido molybdenum(VI) complex with a pendant olefin arm. This goal seemed particularly attractive for the following reason: the SOHIO process is proposed to proceed via O=Mo^{VI}=NH units to which then propene is coordinated before the first H atom abstraction the occurs. A complex containing $O = Mo^{VI} =$ N-C₆H₄-CH₂-CH=CH-CH₃ moiety would thus contain all "ingredients" to model such a situation. We therefore attempted the synthesis of $[Cl_2Mo(=O) (=N-C_6H_4-CH_2-CH=CH-CH_3)(dme)]$ (2), similarly to the synthesis of 1 with only one equivalent of I [compare 13]. This experiment was successful, however, many unidentified by-products formed, which made the work up difficult, so that the yield of 2 was quite low via this procedure. An alternative route reported to provide molybdenum oxo imido compounds [14] proved to be more suitable: the dioxo complex $[(dme)Cl_2Mo(=O)_2]$ was reacted with the diimido compound 1 to give 2 in a commutation reaction (Eq. 4) with an isolated yield of 36 %.



2 was fully characterized, and according to the ¹H NMR spectrum the trans/cis ratio within the ligand **A** amounts to 10.3 : 1. In principle **2** is ideally suited for experiments along the lines described above, i.e. abstraction of an anionic ligand to coordinate the olefinic function of **A** or even additional proton abstraction (\rightarrow altogether HCl elimination) to convert it into an allyl ligand (Eq. 5).



Several experiments were carried out in this respect. Similar systems eliminated HCl after photochemical activation [5], but **2** behaved inert under these conditions. In the next step it was tried to induce the elimination of HCl by adding a suitable (low nucleophilicity, low oxophilicity and hardly any reducing properties) base. However, neither LiNMe₂ (decomposition of **2**) nor NaN(SiMe₃)₂ led to the desired product, and with K₂CO₃ no conversion was observed.

In order to see whether the d^0 configuration or the specific coordination of the starting materials chosen pose the problems preventing the ligand **A** from adopting a chelating binding mode, we finally prepared the cyclopentadienyl Mo^V complex

 $[CpCl_2Mo=N-C_6H_4-CH_2-CH=CH-CH_3]$ (3), via reaction of $[CpMoCl_4]$ with 3 eq. I (Eq. (6)) [15].



After work up **3** was obtained in 90 % yield, and it was characterised by IR spectroscopy, elemental analysis as well as by single crystal X-ray diffraction. The result is shown in Figure 2.

The molecular structure can be described as a threelegged piano-stool. The Mo-N-C6 angle of 163.2° and the Mo-N bond distance of 1.735 Å again point to a Mo=N triple bond, and thus to a 17 electron configuration. Again attempts were made to replace the chloride by methyl ligands via reaction with two equivalents of MeMgI. A colour change from dark purple to dark green could be noticed, and cooling of a pentane solution yielded a dark green solid which, however, proved to decompose rapidly during work up and thus eluded isolation and characteriz-



Figure 2 Molecular structure of complex 3. All hydrogen atoms were omitted for clarity. Selected bond distances /Å and angles /°: Mo-N = 1.735(3), Mo-Cl2 = 2.376(1), Mo-Cl1 = 2.351 (1), N-C6 = 1.393(4), Mo-N-C6 = 163.2 (2).

ation. Hence, in an additional experiment the dark green intermediate was reacted in situ with $B(C_6F_5)_3$ leading to a further colour change to red-brown, but yet again the product was highly sensitive and could not be identified.

Conclusions

Three molybdenum complexes containing the ligand A have been prepared and fully characterized: a diimido complex, 1, a cyclopentadienylimido complex 3, and an oxo/imido compound, 2. 2 is of special interest since it has all prerequisites to model the first step of the SOHIO process, the binding of an olefin to a O=Mo=NH unit with subsequent formation of an allylic ligand. However, the ligand A is obviously not suited to bind to a Mo^{VI} atom in a chelating allyl/N= or olefin/N= mode, especially with the background that the existence of a diimidomolybdenum(π -allyl) complex has been reported [4] so that electronic problems can be excluded. The reasons for that are not quite clear, possibly the tether is chosen to short. Nevertheless, the compounds 1-3 are also interesting in a different context: the grafting of molybdenum complexes on the surfaces of solid supports for the preparation of heterogeneous oxidation catalysts [16]. Only recently many attempts were made to fix CpMo complex metal fragments on surfaces via the co-ligands, in order to obtain heterogeneous epoxidation catalysts [16], and the olefinic function in A should allow for a facile grafting (leaching should be minimal as the imido end forms a very strong bond to molybdenum). In the same context it has to be mentioned that $(RN=)_2M$ compounds were shown to represent active polymerization catalysts after activation [17], and again the olefinic functions in 1 could represent a starting point for grafting.

Experimental Section

General Procedures

All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (¹H 400.13 MHz; ¹³C 100.63 MHz) with CD₂Cl₂ or CD₃CN as solvents at 20 °C. The ¹H and ¹³C NMR spectra were calibrated against the residual proton and natural abundance ¹³C resonances of the deuterated solvent (CD₂Cl₂ $\delta_{\rm H}$ 5.32 ppm or CD₃CN $\delta_{\rm H}$ 1.94). Microanalyses were performed on a Leco CHNS-932 elemental analyser. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR-spectrometer. Melting Points were performed with a Stuart SMP 10.

Materials

Solvents were purified, dried and degassed prior to use. Triethylamine was freshly distilled and degassed, I was degassed and NaMoO₄ was heated at 150 °C and dried in vacuum. [MoO₂Cl₂(dme)] [13], N-(but-3-en-2-yl)aniline, 2-(ⁿbut-2-en-1-yl)aniline [7] were prepared according to the literature procedure.

$[Mo(NC_6H_4CH_2CHCHCH_3)_2Cl_2(dme)] (1)$

To a stirred suspension of 510 mg (2.48 mmol) sodium molybdate in 90 ml dme 730 mg (4.96 mmol) (ⁿbut-2-en-1-yl)amine I and 1.39 ml (9.9 mmol) triethylamine each in 10 ml dme were added. Finally, 2.53 ml (19.8 mmol) chlorotrimethylsilane was added over a period of 5 min, and the resulting reaction mixture was heated 18h at 80 °C. The red solution was cooled to room temperature and filtered to remove the precipitate. The volatile components were removed from the filtrate in vacuo, and the solid residue was recrystallized from toluene/pentane at -30 °C to yield 1.125 g (2.05 mmol, 83 %) dark red crystals.

Elemental analysis for $C_{24}H_{32}Cl_2MoN_2O_2$ (547.4); C 51.58 (calc. 52.66); H 5.86 (5.89); N 5.12 (5.12) %. Concerning the deviation of the C value compare [8].

¹H-NMR (CD₃CN) δ = 1.58 [d, J(H,H)=5.2 Hz, 3H, CH–CH₃], 3.41 [d, J(H,H)=6.0 Hz, 2H, Aryl–CH₂], 3.56 [s, 3H, O–CH₃], 3.72 [s, 2H, O–CH₂], 5.52 [m, 2H, CH–CH–CH₃], 7.02 [td, J(H,H)=5.7, 0.9 Hz, 1H, CH_{ar}], 7.12 [m, 2H, CH_{ar}], 7.21 [d, J(H,H)=6.1 Hz, 1H, CH_{ar}], ¹³C{¹H}–NMR (CD₃CN) δ = 18.0 [CH–CH₃], 35.1 [Aryl–CH₂], 61.6 [br., O–CH₃], 72.3 [O–CH₂], 125.5 [CH–CH₃], 127.1 [CH_{ar}], 127.3 [CH_{ar}], 127.9 [CH_{ar}], 129.7 [CH_{ar}], 130.5 [CH–CH–CH₃], 134.1 [C–CH₂], 156.3 [C–N]. **IR** /cm⁻¹: \tilde{v} = 3035, 3019 (vw), 2936 (w), 2851 (vw), 1584 (w), 1557 (w), 1491 (vw), 1468 (m), 1441 (s), 1375 (vw), 1285 (s), 1188 (m), 1156 (vw), 1109 (m), 1088 (s), 1047 (vs), 1006 (m), 973 (vs), 858 (vs), 826 (m), 798 (w), 764 (vs), 670 (w), 602 (vw).

$[MoO(NC_6H_4CH_2CHCHCH_3)Cl_2(dme)] (2)$

1. To a stirred suspension of 1.399 g (6.8 mmol) sodium molybdate in 90 ml dme 1 g (6.8 mmol) ("but-2-en-1-yl)amine I, 5.72 ml (40.7 mmol) triethylamine and 1.73 ml (13.6 mmol) chlorotrimethylsilane each in 10 ml dme were added. The reaction mixture was stirred 1h at room temperature and additional 6 h at 60 °C. The red solution was cooled to room temperature and filtered to remove the precipitate. The volatile components were evaporated from the filtrate in vacuo yielding a red oil. The product was extracted with 4 x 30 ml diethylether and the solution was reduced in vacuum to 15 ml. The solution was kept at -80 °C overnight and then at -30 °C for a few days. After filtration analytically pure red-orange crystals were obtained in a yield of 368 mg (0.88 mmol, 13 %).

2. To a stirred solution of $712 \text{ mg} (1.3 \text{ mmol}) \mathbf{1}$ in 50 ml dme $376 \text{ mg} (1.3 \text{ mmol}) \text{ MoO}_2\text{Cl}_2(\text{dme})$ were added. The reaction mixture was heated 6h at 85 °C. The volatile components were then removed in vacuum and the product isolated as described above; yield 394 mg (0.94 mmol), 36 %).

Melting Point: 83 °C (decomposition). Elemental analysis for $C_{14}H_{21}Cl_2MoNO_3$ (418.2); C 40.08 (calc. 40.21); H 4.92 (5.06); N 3.21 (3.35); Cl 17.30 (16.96) %.

¹**H-NMR** (CD₂Cl₂) δ = 1.68 [dd, J(H,H)=6.0, 0.8 Hz, 3H, CH–CH₃], 3.79 [d, J(H,H)=6.8 Hz, 2H, Aryl–CH₂], 3.96 [s, 6H, O–CH₃], 4.02 [s, 4H, O–CH₂], 5.59 [m, 1H, CH–CH₃], 5.69 [m, 1H, CH–CH–GH₃], 7.22 [t, J(H,H)=7.2, 1H, CH_{ar}], 7.31 [m, 2H, CH_{ar}], 7.56 [d, J(H,H)=8.0, 1H, CH_{ar}], 1³C{¹H}-**NMR** (CD₂Cl₂) δ = 18.1 [CH–CH₃], 35.0 [Aryl–CH₂], 64.6 [O–CH₃], 72.0 [O–CH₂], 126.9 [CH_{ar}], 127.0 [CHCHCH₋₃], 127.7 [CH_{ar}], 129.6 [CH_{ar}], 129.7 [CH_{ar}], 130.7 [CH–CH–CH₃], 139.6 [C–CH₂], 154.6 [C–N]. **IR** /cm⁻¹: \tilde{v} = 3021 (vw), 2940, 2851 (w), 1584 (m), 1557 (w), 1455 (s), 1443, 1373 (w), 1279 (m), 1240 (s), 1189 (s), 1159 (m), 1119 (w), 1086, 1047 (vs), 970, 923, 862 (s), 826, 779 (m), 731, 710, 661, 586 (w), 503, 541, 517 (m).

$[(C_5H_5)Mo(NC_6H_4CH_2CHCHCH_3)Cl_2] (3)$

To a stirred suspension of 500 mg (1.65 mmol) (C_5H_5)MoCl₄ in 30 ml toluene 729 mg (4.95 mmol) ("but-2-en-1-yl)amine I in 20 ml

	1	3
formula	C24H32Cl2MoN2O2	C15H16Cl2M0N
weight, $g \cdot mol^{-1}$	547.36	377.13 g/mol
temp, K	150(2) K	150(2) K
wavelength, Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic
space group	C2c	$P2_1/c$
a, Å	18.18(12)	10.426(2)
b, Å	10.78(2)	7.7594(10)
c, Å	13.57(4)	19.316(4)
β, deg	103.3(4)	91.22(2)
V, Å ³	259(2)	1562.3(5)
Z	4	4
density, $g \cdot cm^{-3}$	1.406	1.603
$\mu(Mo_{K\alpha}), mm^{-1}$	0.736	1.167
F(000)	1128	756
GoF	1.173	1.058
$R_1 [I > 2\sigma(I)]$	0.1523	0.0337
wR_2 (all data)	0.3003	0.0864
$\Delta \rho_{\rm min} / \Delta \rho_{\rm max}$, eÅ ⁻³	-0.566/0.733	-0.926/0.725

Table 1Crystal data and details for the crystal structure refinement of 1 and 3.

toluene were added over a period of 5 min. The reaction mixture was stirred for 2h at room temperature. The solvent was removed in vacuo, and the product was extracted with 4 x 30 ml dietylether from the ammonium salt of I formed as a byproduct. The solution was evaporated in vacuum to 15 ml and 50 ml of pentane were added. After a few days at -30 °C 764 mg (1.50 mmol, 90 %) dark purple crystals were obtained.

Elemental analysis for $C_{15}H_{16}Cl_2MoN$ (377.14); C 47.89 (calc. 47.77); H 4.35 (4.28); N 3.70 (3.71); Cl 18.83 (18.80) %.

 $\mathbf{IR}\ /\mathrm{cm}^{-1}: \tilde{\nu} = 3100\ (vw),\ 2919,\ 2848,\ 2359,\ 2334,\ 2331,\ 1584,\ 1493\ (w),\ 1468\ (s),\ 1442\ (m),\ 1437,\ 1417\ (vs),\ 1377\ (w),\ 1294\ (m),\ 1262,\ 1157,\ 1112,\ 1101,\ 1062\ (w),\ 1034\ (s),\ 1018,\ 991\ (m),\ 969\ (s),\ 855\ (m),\ 836\ (s),\ 821\ (vs),\ 804,\ 767\ (s),\ 668\ (w).$

Crystal Structure Determinations

Single crystals of 1 (disordered) were obtained by overlayering a solution of 1 in dichloromethane with pentane at -30 °C. Single crystals of 3 were obtained by overlayering a solution of 3 in diethylether with pentane at -30 °C. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the diffractometer (Stoe STADI 4 (1) and Stoe IPDS (3)) using Mo_{Kα} radiation, $\lambda = 0.71073$ Å, and both structures were solved by direct methods (SHELXS-97) [18], refined versus F^2 (SHELXL-97) [19] with anisotropic temperature factors for all non-hydrogen atoms (Table 1). All hydrogen atoms were added geometrically and refined by using a riding model.

The crystallographic data (apart from structure factors) of **1** and **3** were deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 289393 (1) and 289392 (3). Copies of the data can be ordered free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (FAX: (+44)1223-336-033; E-mail: **deposit@ccdc.cam.ac.uk**).

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References

- [1] J. D. Idol, US Patent 2 1959, 904, 580.
- [2] S. P. Lankhuyzen, P. M. Florack, H. S. v. d. Baan, J. Catal. 1976, 42, 20; R. K. Graselli, J. D. Burrington, J. F. Bradzil, Farad. Discuss. 1981, 72, 203; J. D. Burrington, C. T. Kartisek, R. K. Grasselli, J. Catal. 1983, 81, 489; R. K. Graselli, J. D. Burrington, Ind. Eng. Chem. Prod. Res. Dev. 1984, 23, 394; C. Limberg, Angew. Chem. 2003, 115, 6112; Angew. Chem. Int. Ed. 2003, 42, 5932.
- [3] M. L. H. Green, P. C. Konidaris, P. Mountford, J. Chem. Soc., Dalton Trans. 1994, 2975.
- [4] U. Radius, J. Sundermeyer, K. Peters, H. G. v. Schnering, Z. Anorg. Allg. Chem. 2002, 628, 1226.
- [5] C. Wippert Rodrigues, B. Antelmann, C. Limberg, H. Pritzkow, Organometallics 2001, 20, 1825.
- [6] R. A. Eikey, M. M. Abu-Omar, *Coord. Chem. Rev.* 2003, 243, 83; W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* 1980, 31, 123; D. E. Wigley, *Prog. Inorg. Chem.* 1994 (42) 239 and ref. cit.
- [7] S. Jolidon. H.-J. Hansen, Helv. Chim. Acta 1977, 60, 978.
- [8] H. H. Fox, K. B. Yap, J. Robbins, S. Cai, R. R. Schrock, *Inorg. Chem.* 1992, 31, 2287.
- [9] R. C. B. Copley, P. W. Dywer, V. C. Gibson, J. A. K. Howard, E. L. Marshall, W. Wang, B. Whittle, *Polyhedron* 1996, 15, 3001.
- [10] V. C. Gibson, C. Redshaw, G. L. P. Walker, J. A. K. Howard, V. J. Hoy, J. M. Cole, L. G. Kuzmina, D. S. De Silva, J. Chem. Soc., Dalton Trans. 1999, 161.
- [11] X. Yang, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 1994, 116, 10015.
- [12] J.-F. Carpentier, Z. Wu, C. W. Lee, S. Strömberg, J. N. Christopher, R. F. Jordan, *J. Am. Chem Soc.* 2000, *122*, 7750; C. P. Casey, D. W. Carpenetti II, *Organometallics* 2000, *19*, 3970.
- [13] K. A. Rufanov, D. N. Zarubin, N. A. Ustynyuk, D. N. Gourevitch, J. Sundermeyer, A. V. Churakov, J. A. K. Howard, *Polyhedron* 2001, 20, 379.
- [14] A. Galindo, F. Montilla, A. Pastor, E. Carmona, *Inorg. Chem.* 1997, 36, 2379.
- [15] M. L. H. Green, P. C. Konidaris, P. Mountford, J. Chem. Soc., Dalton Trans. 1994, 2851.
- [16] A. Sakthivel, J. Zhao, M. Hanzlik, F. E. Kühn, *Dalton Trans.* 2004, 3338; A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, M. Hanzlik, A. S. T. Chiang, F. E. Kühn, *Appl. Catal. A* 2005, 281, 267.
- [17] M. P. Coles, C. I. Dalby, V. C. Gibson, W. Clegg, M. R. J. Elsegood, J. Chem. Soc., Chem. Commun. 1995, 1709; M. P. Coles, V. C. Gibson, Polym. Bull. 1994, 33, 529.
- [18] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, 1997.
- [19] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure R efinement, University of Göttingen, 1997.