

Bis(cyclopentadienyl) Diimido Complexes of Molybdenum and Tungsten [Cp₂M(NR)₂] at the Limit of Pi-Bond Saturation

Udo Radius,^[a] Jörg Sundermeyer,^{*[b]} Karl Peters,^[c] and Hans-Georg von Schnering^[c]

Dedicated to Professor Max Schmidt on the occasion of his 75th birthday

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The new imido compounds [(η⁵-C₅H₅)M(NR)₂(η¹-C₅H₅)] (R = *t*Bu: M = Mo **2a**, W **2b**; R = Mes: M = W **2c**) have been prepared and the crystal structure of **2c** has been determined. Three fluxional processes can be detected by variable temperature proton NMR spectroscopic studies of these cyclopentadienyl complexes, namely: (i) rotation of the σ-C₅H₅ li-

gand about the M–C_{ipso}-bonding axis, (ii) migration of the metal complex fragment between the carbon atoms of the σ-bonded C₅H₅ ligand (metallotropic migration, sigmatropic rearrangement), and (iii) the interconversion of hapticity of σ- and π-bonded C₅H₅ ligands.

Introduction

Molybdenum(VI) and tungsten(VI) bis(organyl) imido complexes of the type [M(NR)₂R¹R²] (M = Mo, W) have been known for twenty years.^[1,2] In the early eighties, the imido-bridged compounds [M(N*t*Bu)(μ-N*t*Bu)(CH₃)₂]₂ were synthesized and characterized by Nugent and co-workers as the first examples of unsymmetrically bridged dinuclear imido compounds. Mononuclear complexes can be obtained by increasing the steric demand of the organyl ligand of the imido compound. Wilkinson et al.,^[3] for example, reported the syntheses of symmetrically substituted bis(aryl) derivatives (R = *t*Bu, R¹ = R² = mesityl, *o*-tolyl), whereas bis(neopentyl) compounds, like those prepared by the groups of Schrock and Osborn,^[4] are attractive starting materials for the synthesis of high valent alkylidene complexes.

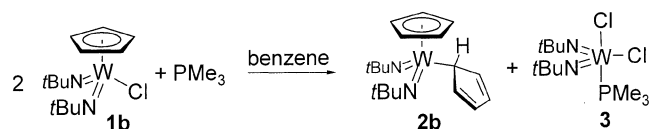
Important intermediates for unsymmetrically substituted bis(organyls) (R¹ ≠ R²) are monoorganyl complexes of the type [M(NR)₂R¹Cl]. During our studies on reactive, N-basic [Mo=NR] and [W=NR] functionalities, we intended to reduce the Lewis acidity of the metal centers of imido complexes [M(NR)₂Cl₂] by introducing excellent σ,π donor ligands. This can be achieved by a formal exchange of a [M–Cl] functionality by [M(η⁵-C₅R'₅)] (R' = H, CH₃).^[5] Complexes of the type [(η⁵-C₅H₅)M(N*t*Bu)₂Cl] or mixed substituted organyl complexes of the type [(η⁵-C₅H₅)M(N*t*Bu)₂R²] (R² = alkyl, aryl)^[5] are no longer typical d-metal Lewis acids.^[6] Here we wish to report the syntheses, molecular structure and dynamic behavior of the

highly π-bond saturated bis(cyclopentadienyl) complexes [(η⁵-C₅H₅)M(NR)₂(η¹-C₅H₅)].

Results and Discussion

Complex Synthesis

The cyclopentadienyl imido complexes [(η⁵-C₅H₅)M(N*t*Bu)₂Cl] (M = Mo **1a**; M = W **1b**) were reacted with typical Lewis bases in order to probe the Lewis acidity of these compounds. Reaction of trimethylphosphane with [(η⁵-C₅H₅)W(N*t*Bu)₂Cl] (**1b**) led to an orange colored solid and a brownish oil. One of the products, [W(N*t*Bu)₂Cl₂(PMe₃)] (**3**),^[7] was identified by ³¹P NMR spectroscopy, but no phosphorus resonance was obtained for the second product. The proton NMR spectrum of the oily residue shows one sharp singlet in the *t*Bu imido region at approximately δ = 1.2, and a very broad resonance in the cyclopentadienyl region. The integration of both signals shows a ratio of 9:5. These experimental results are in accordance with a ligand *dismutation* of [(η⁵-C₅H₅)W(N*t*Bu)₂Cl] (**1b**) to give [(C₅H₅)₂W(N*t*Bu)₂] (**2b**) and [W(N*t*Bu)₂Cl₂] by a phosphane-induced exchange of a chloride and a cyclopentadienyl ligand. The latter Lewis acid is trapped by the phosphane to yield [W(N*t*Bu)₂Cl₂(PMe₃)] (**3**).



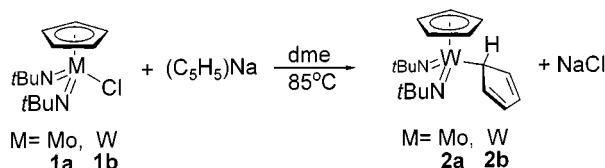
Green and co-workers observed a similar unexpected substitution reaction of a cyclopentadienyl ligand, with stabilization of the resulting Mo^{IV} species, whilst studying the reduction reactions of [(η⁵-C₅H₄Me)Mo(N*t*Bu)Cl₂] in the presence of phosphanes.^[8]

^[a] Institut für Anorganische Chemie, Engesserstr., Geb. 30.45, 76128 Karlsruhe, Germany
E-mail: uradius@achim6.chemie.uni-karlsruhe.de

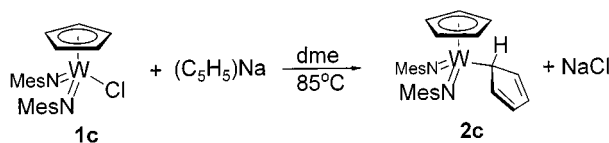
^[b] Fachbereich Chemie der Universität Marburg, Hans-Meerweinstraße, 35032 Marburg, Germany
E-mail: jsu@chemie.uni-marburg.de

^[c] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70506 Stuttgart, Germany

To confirm the results of this rather unusual displacement of an anionic C_5H_5 ligand by a phosphane, we prepared **2b** independently. All experiments to obtain **2b** or its molybdenum analogue $[(C_5H_5)_2Mo(NtBu)_2]$ **2a**, by reaction of the chloro complexes $[(\eta^5-C_5H_5)M(NtBu)_2Cl]$ **1a,b** with $(C_5H_5)Li$ were unsuccessful. However, refluxing **1a,b** with $(C_5H_5)Na$ in dimethoxyethane for several hours led to the formation of the bis(cyclopentadienyl) compounds $[(C_5H_5)_2M(NtBu)_2]$ **2a,b** isolated as yellow-brown oils. These highly covalent organo imides **2a,b** can be purified by high-vacuum distillation or condensation.



As we were not able to obtain crystalline material of the *tert*-butyl imido complexes **2a,b** by low temperature crystallization techniques, we synthesized the corresponding mesityl imido tungsten complex $[(C_5H_5)_2W(NMes)_2]$ (**2c**). This complex can also be obtained from the reaction of $[(C_5H_5)W(NMes)_2Cl]$ (**1c**) with sodium cyclopentadienide in dimethoxyethane. Single crystals of **2c** were grown by the slow cooling of saturated hexane solutions of **2c** to $-60^\circ C$.



Molecular Structure of **2c**

$[(C_5H_5)_2W(NMes)_2]$ (**2c**) crystallizes in the triclinic space group $P\bar{1}$. The molecular structure is shown in Figure 1. Selected bond lengths and angles are given in the caption. Further details of the crystallographic characterization are given in Table 1.

$[(C_5H_5)_2W(NMes)_2]$ (**2c**) is a monomer in the solid state. The tungsten atom is pseudotetrahedrally coordinated by the two imido nitrogen atoms, by the coordinating carbon atom of a σ -bonded cyclopentadienyl ligand, and by the centroid of a π -coordinated cyclopentadienyl unit. The bonding angles $N(1)-W-N(2)$ $107.7(2)^\circ$, $N(1)-W-C(6)$ $97.3(2)^\circ$, and $N(2)-W-C(6)$ $99.7(2)^\circ$ reflect some distortion of the coordination polyhedron. The $W-N$ bond lengths of 176.6(4) pm and 175.9(4) pm are consistent, to some degree, with tungsten imido-nitrogen triple bonding, corresponding to a bond order of 2.5^[9a] and comparable with that of the π -bond saturated complex $[W(NPh)(NMe_2)_4]$ [$W-N(\text{imido}) = 175.8(5)$].^[9b] The $W-C(6)$ distance of 220.0(6) pm is in the range of tungsten(VI)-carbon σ -bonds. The tungsten-carbon bond lengths of the π -coordinated cyclopentadienyl ring show some interesting irregularities: $W-C(1)$ [233.4(6) pm] falls into the range of expected tungsten ring carbon bond

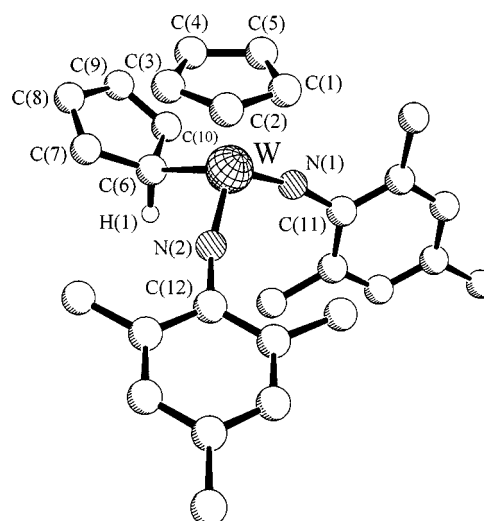


Figure 1. Molecular structure of **2c** in the solid state; SCHAKAL^[27] plot; hydrogen atoms are omitted for clarity; selected bond lengths (pm) and angles ($^\circ$): $W-N(1)$ 176.6(4), $W-N(2)$ 175.9(4), $W-C(1)$ 233.4(6), $W-C(2)$ 244.0(6), $W-C(3)$ 250.2(6), $W-C(4)$ 247.4(6), $W-C(5)$ 241.6(6), $W-C(6)$ 220.0(6), $N(1)-C(11)$ 138.7(7), $N(2)-C(12)$ 139.2(6), $C(1)-C(5)$ 139.9(8), $C(1)-C(2)$ 140.4(10), $C(2)-C(3)$ 139.6(9), $C(3)-C(4)$ 139.9(9), $C(4)-C(5)$ 137.2(11), $C(6)-C(7)$ 149.1(9), $C(7)-C(8)$ 133.5(10), $C(8)-C(9)$ 142.6(11), $C(9)-C(10)$ 136.5(12), $C(6)-C(10)$ 146.5(8); $N(1)-W-N(2)$ 107.7(2), $N(1)-W-C(6)$ 97.3(2), $W-N(1)-C(11)$ 164.4(3), $W-N(2)-C(12)$ 166.8(4), $N(2)-W-C(6)$ 99.7(2)

lengths,^[9c] whereas the distances $W-C(5)$ [241.6(6) pm], $W-C(2)$ [244.0(0) pm], $W-C(3)$ [250.2(6) pm], and $W-C(4)$ [247.4(6) pm], are significantly elongated. Comparable elongations of the $W-C(\text{ring})$ bonds trans to strong π -donor ligands have been observed by Bercaw et al. for $[(\eta^5-C_5Me_5)W(O)_2(O-C_5Me_5)]$ and $[(\eta^5-C_5Me_5)W(O)_2(\eta^1-C_5Me_5)]$, and were attributed to the *trans* influence of the oxo ligands.^[10] We have observed similar effects in the structurally characterized half-sandwich imido complex $[(\eta^5-C_5Me_5)Mo(NtBu)Cl_3]$,^[5c] but they are also characteristic for the nitrosyl compounds of the type $[(\eta^5-C_5H_5)_2Mo(NO)R]$ ($R = \text{alkyl}$)^[11] and for the metallocene imido derivatives $[(\eta^5-C_5H_5)_2V(N\text{otol})]$ ^[12] and $[(\eta^5-C_5H_4Me)_2Mo(NtBu)]$.^[13] Calculations on the latter 19 and 20 valence electron (VE) complexes show that the HOMO of these compounds is a ligand-centered orbital with significant contributions to the nitrogen atoms of the imido group and to the π -system of the cyclopentadienyl units. In a MO bond description, one of the p orbitals located on the imido nitrogen atoms competes with the two group orbitals of π -symmetry (e_1) of the η^5 -coordinated ring for stabilization with one empty d orbital located on the metal center. As a result, a high degree of metal-nitrogen bonding (e.g. $M-N$ triple bond contributions) leads to a decrease in metal-cyclopentadienyl π -bonding, and thus to a ring slippage of the $\eta^5-C_5R_5$ ring.

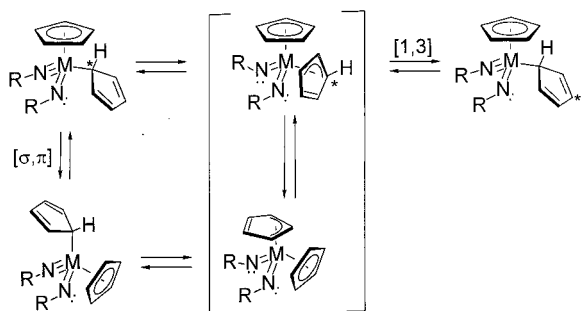
Variable Temperature 1H NMR Spectra

The proton NMR spectra of the compounds $[(C_5H_5)_2M(NR)_2]$ **2a-c** are temperature dependant. Three

Table 1. Crystal Structure Analysis of **2c**

Compound	[Cp ₂ W(NMes) ₂]
Empirical formula	C ₂₈ H ₃₂ N ₂ W
Molecular mass	580.43
<i>a</i> [pm]	1005.7(1)
<i>b</i> [pm]	1606.5(3)
<i>c</i> [pm]	806.7(1)
α [deg]	98.55(1)
β [deg]	94.43(1)
γ [deg]	105.54(1)
<i>V</i> [pm ³]	1232.3(3) × 10 ⁶
<i>Z</i>	2
<i>d</i> (calcd) [g·cm ⁻³]	1.564
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Diffractometer	Siemens R3m/V
Radiation	Mo- <i>K</i> α
Monochromator	graphite
Crystal size [mm]	0.2 × 0.45 × 0.75
Data collection mode	ω -scan
Theta range [deg]	1.75–27.5
Recip. latt. segment	<i>h</i> = 0 → 13 <i>k</i> = –20 → 19 <i>l</i> = –10 → 10
No. refl. Measd.	5663
No. unique refl.	5663
No. refl. <i>F</i> > 3 σ (<i>F</i>)	4977
Lin. abs. coeff. [mm ⁻¹]	4.70
Abs. Correction	ψ -scan
Solution by	Direct phase determination
Method of refinement	Full-matrix LSQ; hydrogen positions of riding model with fixed isotropic <i>U</i>
Data-to-parameter ratio	17.71
<i>R</i> , <i>R</i> _w	0.031, 0.030
Weighting scheme	<i>w</i> = 1/ σ^2 (<i>F</i>)
Largest difference peak	1.80 eÅ ⁻³
Largest difference hole	1.15 eÅ ⁻³
Program used	Siemens SHELXTL PLUS: G. M. Sheldrick, Program package SHELXTL-PLUS, Release 4.1, Siemens Analytical X-ray Instruments Inc., Madison, WI 53719, USA, 1990

dynamic processes, which have been observed previously in solutions of other η^1/η^5 bis(cyclopentadienyl) complexes, are responsible for this dynamic behavior (see Scheme 1), namely: (i) hapticity change of σ - and π -coordinated cyclopentadienyl rings, (ii) metallotropic migration of the frag-



Scheme 1. Hapticity change and mechanistic proposal of a metallotropic rearrangement via allyl intermediates in complexes of the type $[\eta^5\text{-C}_5\text{H}_5]\text{M}(\text{NR})_2(\eta^1\text{-C}_5\text{H}_5)$ (*M* = Mo, W)

ment $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NR})_2]$ between the carbon atoms of the monohapto-coordinated cyclopentadienyl ring, and (iii) rotation of the σ -cyclopentadienyl ligand around the *M*–C_{ipso} bonding axis.

The cyclopentadienyl region between $\delta = 4.0$ and 8.5 in the proton NMR spectra of $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{N}t\text{Bu})_2]$ (**2a**), recorded at different temperatures, is shown in Figure 2. At 363 K, the ¹H NMR spectrum of **2a** shows one averaged signal at $\delta = 5.78$ assigned to the cyclopentadienyl protons and a resonance at $\delta = 1.13$ assigned to the protons of the imido group (not shown in Figure 2), with a ratio of integration of 5:9. On cooling the signal of the *tert*-butyl imido group remains constant within experimental error, while the cyclopentadienyl resonance broadens and splits into two signals below the coalescence temperature of 308 K. At 283 K, two broad signals of similar width are detectable [$\Delta G^\ddagger(308\text{ K}) = 61.0\text{ kJ/mol}$]. The signal at $\delta = 6.26$ is assigned to the protons of the η^1 -coordinated cyclopentadienyl ring due to its chemical shift^[15] and the characteristic splitting at lower temperatures. The resonance at higher field ($\delta = 5.33$) can be assigned to the protons of the η^5 -coordinated cyclopentadienyl ligand. A further decrease in the temperature from 308 K (the point of coalescence for the σ/π exchange) to 196 K (the point of coalescence for the metallotropic rearrangement) leads to a broadening of the resonance at $\delta = 6.26$ and to a

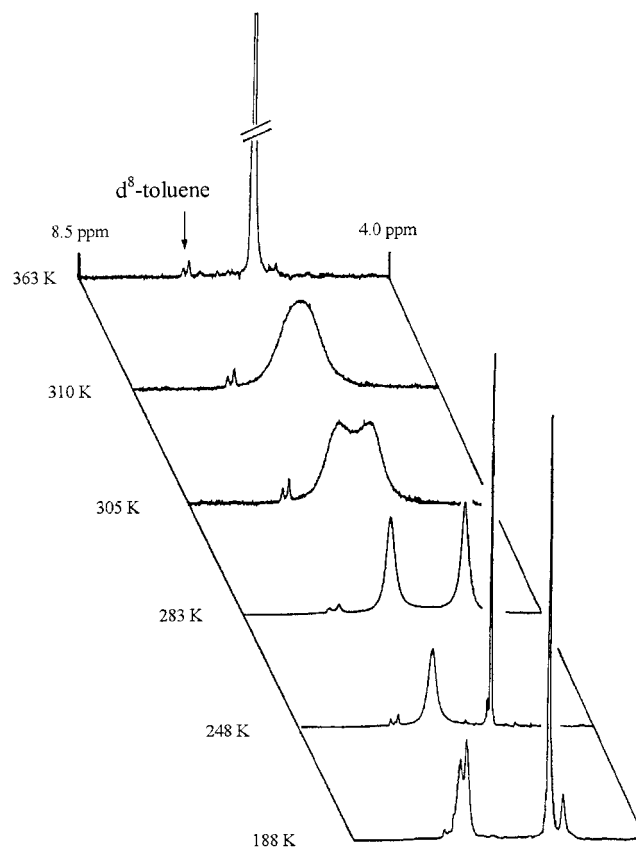


Figure 2. Variable temperature proton NMR spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{N}t\text{Bu})_2(\eta^1\text{-C}_5\text{H}_5)]$ (**2a**) in $[\text{D}_8]\text{toluene}$ showing the C_5H_5 region from $\delta = 4.00$ to 8.50

sharpening of the η^5 -cyclopentadienyl resonance. Below this second coalescence temperature of 196 K, the signal of the η^1 -C₅H₅ group splits into two resonances for the olefinic protons at $\delta = 6.82$ and 6.71 (at 188 K), and one signal at $\delta = 5.05$ for the proton of the CH group bound to the metal atom, as expected for a not-yet-resolved AA'BB'X spin-spin system.

Similar spectra can be recorded for the tungsten compound [(C₅H₅)₂W(NtBu)₂] (**2b**). The coalescence temperature for σ, π exchange is slightly higher for the tungsten complex **2b** [$\Delta G^\ddagger(310\text{ K}) = 64.4\text{ kJ/mol}$] than for the molybdenum analogue **2a**.

The temperature-dependent ¹H NMR spectra of the tungsten compound [(C₅H₅)₂W(NMes)₂] (**2c**) offer some peculiarities. At a relatively high coalescence temperature of 328 K [compared with the *tert*-butyl derivatives **2a** (308 K) and **2b** (310 K)], the resonance for the cyclopentadienyl protons of **2c** splits into two signals at $\delta = 6.25$ and 5.47. By lowering the temperature, the signal at $\delta = 6.25$ further splits into a set of five resonances. They are assigned to the vinylic protons of **2c** H_{A/A'} ($\delta = 7.01$ and 6.90) and H_{B/B'} ($\delta = 6.57$ and 6.55) and to the proton H_X at the *ipso* carbon ($\delta = 6.57$). At 210 K coalescence of the vinylic pairs of protons is observed. In the low temperature limiting spectrum at 193 K, every proton of the η^1 -coordinated cyclopentadienyl ligand is chemically inequivalent indicating that at very low temperatures the rotation about the metal *ipso*-carbon bond as a third dynamic process, besides the hapticity change and the metallotropic migration, is slowly resolved on the NMR time scale. The significantly higher coalescence temperature for the mesityl complex **2c** than for **2a, b** may be explained by the higher mass and by the increased steric demand of the migrating group [(η^5 -C₅H₅)₂W(NMes)₂] compared with [(η^5 -C₅H₅)₂M(NtBu)₂] (M = Mo, W). In a similar manner it has been reported by Werner et al.^[16] that the rate of the σ/π exchange in [(η^5 -C₅H₅)Pd(η^1 -C₅H₅)(PR₃)] is dependant on the cone angle^[17] of the phosphane ligand PR₃.

Mechanistic Considerations

Hapticity Change

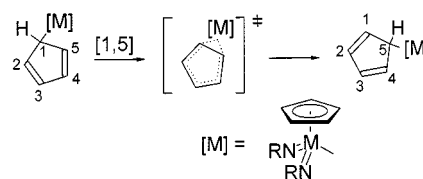
The exchange reaction between σ - and π -bonded cyclopentadienyl ligands has been well investigated, for example, for [(η^5 -C₅H₅)₃Ti(η^1 -C₅H₅)],^[18] [(η^5 -C₅H₅)₂Mo(η^1 -C₅H₅)(NO)],^[11] [(η^5 -C₅H₅)Mo(η^1 -C₅H₅)(S₂CNR₂)₂] (R = Me, Bu),^[19] [(η^5 -C₅H₅)Pd(η^1 -C₅H₅)(PiPr₃)],^[16] [(η^5 -C₅H₅)V(NtBu)(η^1 -C₅H₅)(OrBu)],^[20] and [(η^5 -C₅H₅)₂Nb(NtBu)(η^1 -C₅H₅)].^[21] Scheme 1 shows a mechanistic proposal for the hapticity change in the imido compounds [(C₅H₅)₂M(NR)₂] (M = Mo, W).

As observed in other molecular compounds with η^1 - and η^5 -coordinating cyclopentadienyl ligands, for example in [(η^5 -C₅H₅)₂Mo(η^1 -C₅H₅)(NO)],^[11] a stepwise or concerted hapticity change is promoted by additional, electronically flexible ligands. The reduction of the imido ligand bond order (BO) from a six VE donor [NR]²⁻ (BO = 3) to a four VE donor [NR]²⁻ (BO = 2) makes the slippage of an η^1 -

bonded cyclopentadienyl ligand to η^3 -coordination more easy, thus it might initiate the exchange from an η^1 - via η^3 - to an η^5 -coordination. A similar flexibility is characteristic for the NO ligand. A mechanism as proposed in Scheme 1 via intermediates of the type [(η^5 -C₅H₅)(η^3 -C₅H₅)M(NR)₂] has been observed for [(C₅H₅)₂W(CO)₂], in which one cyclopentadienyl ligand adopts an η^3 -, and the other one an η^5 -coordination mode.^[22]

Metallotropic Migration

Over the last 40 years a large number of η^1 -C₅H₅ compounds of main group elements and transition metals have been described.^[23] Whilst the migration of the metal substituent between the ring carbon atoms has recently been recognized as an intramolecular process,^[24] the exact mechanism of the metallotropic rearrangement has remained an unresolved problem for some time. Conclusions were finally drawn from statistical considerations of the different processes under consideration (1,2 shift vs. 1,3 shift vs. random walk) and the initial broadening of the resonances of the vinyl protons below coalescence temperature. Investigations with prochiral complex fragments finally established the [1,2]-metallotropic migration (see Scheme 2) as the energetically most favorable mechanism.^[25] The latter may be regarded as a symmetry-allowed [1,5]-sigmatropic rearrangement.



Scheme 2. [1,2]-metallotropic migration as [1,5]-sigmatropic rearrangement

According to Cotton and co-workers,^[25] [1,2]-migration can be identified by a preferred broadening of the signals of H_{A/A'} below the coalescence temperature of this process, while a [1,3]-shift can be detected by a preferred broadening of the resonances of H_{B/B'}. The proton NMR spectra of **2c** in the relevant temperature range between 220 K and 260 K show a larger broadening for the H_{A/A'} and H_X signals than for H_{B/B'}. This is in agreement with a nonrandom mechanism of the metallotropic rearrangement, and the qualitative consideration indicates a [1,2] shift of the molybdenum or tungsten center between the carbon atoms of the σ -(C₅H₅) ligand. It seems that a concerted [1,5]-sigmatropic rearrangement has a lower energy barrier than the formation of an allylic intermediate. However, due to the flexibility in the electron count of the imido ligand it cannot be excluded that, at higher temperatures, both the [1,2]- and the energetically less favorable [1,3]-migration might contribute to the metallotropic migration. We examined the possibility of determining rate constants of the low temperature rearrangements by recording the spectra at higher frequency; how-

ever, the rather complex exchange system turned out to be intractable by the methods available to us.

Conclusions

The new imido complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NR})_2(\eta^1\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}, \text{W}$, $\text{R} = t\text{Bu}$; $\text{M} = \text{W}$, $\text{R} = \text{Mes}$) **2a–c** have been prepared. Although the metal atoms of the bis(organyl) compounds **2a–c** are in their highest formal oxidation state, the Lewis acidity of the d^0 metal centers is well compensated by both types of the excellent σ -, 2π -donor ligands $[\text{NR}]^{2-}$ and $[\text{C}_5\text{H}_5]^-$. The compounds **2a–c** are π -bond saturated. That means two potential π -bonds of each C_5H_5 ligand (e_1 group orbitals of C_5H_5) and two potential π -bonds of each imido ligand (p orbitals of N atoms) add to a number exceeding the maximum of five π -bonds theoretically possible from orbital symmetry considerations in tetrahedral transition metal complexes.^[26] It has been proven that in their competition for π -bonding with the d^0 metal acid, the stronger π -donors $[\text{NR}]^{2-}$ are driving the weaker π -donors $[\text{C}_5\text{H}_5]^-$ out of the π -coordination. Therefore, these complexes may be considered as 18 VE complexes of a d^0 metal center stabilized by four σ -bonds to two C_5H_5 and to two imido ligands, as well as by five π -bonds, two to the $\eta^5\text{-C}_5\text{H}_5$ ligand and three π -bonds to both imido ligands, leading to an average bond order of 2.5. This consideration implies that a certain amount of π -electron density remains in ligand-centered nonbonding orbitals. Structural data and the σ, π dynamic behavior of the compounds **2a–c** in solution are consistent with this conclusion. The stronger π -donor ability of imido vs. cyclopentadienyl ligands at a d^0 metal center has also been demonstrated by Green et al. for the isolobally related niobium compound $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{N}t\text{Bu})(\eta^1\text{-C}_5\text{H}_5)]$.^[21] Due to the electronic flexibility of the four vs. six electron imido ligand $[\text{NR}]^{2-}$, an allylic species $[(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{M}(\text{NR})_2]$ ($\text{M} = \text{Mo}, \text{W}$) might be considered as an intermediate of the η^5/η^1 exchange process and for the metallotropic [1,3] migration; however, as in the related niobium imido complex, the [1,2]-metallotropic rearrangement is the dominant mechanism in the dynamic behavior at the low temperature limit.

Experimental Section

General: All reactions and subsequent manipulations involving organometallic reagents were performed under argon (4.8) using standard Schlenk techniques. Solvents were dried according to standard procedures, stored over activated 4 Å molecular sieves and degassed prior to use. – Melting and decomposition points were determined in closed capillaries on a Büchi SMP 20 or as DTAs on a duPont 9000 apparatus. – Infrared spectra were recorded as Nujol mulls on KBr windows on a Bruker IFS 25 – NMR spectra were recorded on a Jeol FX90Q, a Bruker AC 200 and a Bruker AMX400 spectrometer. – $[\text{W}(\text{NMe})_2\text{Cl}_2(\text{dme})]$ ($\text{M} = \text{Mo}, \text{W}$)^[6] and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NR})_2\text{Cl}]$ ^[5a] were prepared as described in the literature.

Chloro(cyclopentadienyl)bis(mesitylimido)tungsten(VI) (1c): $[\text{W}(\text{NMe})_2\text{Cl}_2(\text{dme})]$ (600 mg, 0.96 mmol) was added at -78°C to a suspension of $\text{C}_5\text{H}_5\text{Li}$ (72.0 mg, 1.00 mmol) in 50 mL diethyl ether. The yellow solution was brought to room temperature within 30 minutes. After 2 h at room temperature, all volatiles were removed and the residue was dried at 50°C in vacuo and finally extracted into 15 mL toluene. The dark red extract was concentrated to 3 mL. On addition of 15 mL hexane, a red solid precipitated, which was collected and dried in vacuo. – Yield: 333 mg (75%); dec.: 101°C – IR (nujol): $\tilde{\nu} = 3104$ w $\nu(\text{C-H}_{\text{ar}})$, 1600 m $\nu(\text{C}=\text{C})$, 1348 s, 1320 vs and 1288 vs $\nu(\text{W}=\text{N}-\text{C})$, 1036 w, 1006 w, 988 m, 936 m, 856 m, 812 s $\nu(\text{C-H}_{\text{ar}})_{\text{oop}}$, 724 m, 504 w, 460 m, 424 cm^{-1} . – ^1H NMR (200.1 MHz, CDCl_3): $\delta = 2.32$ (s, 18 H, Mes- CH_3), 6.56 (s, 5 H, C_5H_5), 6.84 (s, 4 H, Mes- H). – ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 18.70$ (s, $o\text{-CH}_3$), 20.69 (s, $p\text{-CH}_3$), 109.64 (s, C_5H_5), 127.74 (s, Mes- $\text{C}3$), 131.16 (s, Mes- $\text{C}2$), 133.46 (s, Mes- $\text{C}4$), 152.73 (s, $^2J_{\text{WC}} = 33.3$ Hz, Mes- $\text{C}1$). – EI-MS: m/z (%) = 550 (100) $[\text{M}^+]$, 485 (67) $[\text{M}^+ - \text{C}_5\text{H}_5]$. – $\text{C}_{23}\text{H}_{27}\text{ClN}_2\text{W}$ (550.8): calcd. C 50.16, H 4.94, N 5.09; found C 49.69, H 5.06, N 5.03.

Bis(tert-butylimido)bis(cyclopentadienyl)molybdenum(VI) (2a): Finely powdered **1a** (339 mg, 1.00 mmol) was added to a suspension of $(\text{C}_5\text{H}_5)\text{Na}$ (106 mg, 1.20 mmol) in 20 mL 1,2 dimethoxyethane at -50°C . The orange colored mixture was brought to room temperature within 30 min. and refluxed for 6 h. All volatiles of the reddish brown suspension were removed in vacuo and the brown, oily residue was extracted with 20 mL hexane. The evaporated hexane extract was distilled at 6×10^{-3} mbar onto a cooled finger (-30°C). The product separated as an orange-brown solid at the finger, which melted at room temperature to give a brown oil. – Yield: 229 mg (63%). – IR (film): $\tilde{\nu} = 3084$ m $\nu(\text{C-H}_{\text{ar}})$, 2968 s, 2920 s, 2892 s, 2860 m, 1696 w, 1660 w, 1588 m $\nu(\text{C}=\text{C})$, 1440 m, 1356 s, 1248 vs and 1216 vs $\nu(\text{Mo}=\text{N}-\text{C})$, 1116 m, 1080 m, 1020 m, 964 m, 888 w, 840 m, 800 vs and 736 s $\nu(\text{C-H}_{\text{ar}})_{\text{oop}}$, 632 w, 584 w, 548 w, 464 cm^{-1} . – ^1H NMR (89.6 MHz, C_7D_8 , 188 K): $\delta = 1.15$ (s, 18 H, NCCCH_3), 5.05 (br, 1 H, $\eta^1\text{-H}_X$), 5.30 (s, 5 H, $\eta^5\text{-C}_5\text{H}_5$), 6.71 (br, 2 H, $\eta^1\text{-H}_{\text{B/B'}}$), 6.82 (br, 2 H, $\eta^1\text{-H}_{\text{A/A'}}$); (89.6 MHz, C_7D_8 , 283 K): $\delta = 1.14$ (s, 18 H, NCCCH_3), 5.33 (s, 5 H, $\eta^5\text{-C}_5\text{H}_5$), 6.29 (br, 5 H, $\eta^1\text{-C}_5\text{H}_5$); (89.6 MHz, C_7D_8 , 363 K): $\delta = 1.13$ (s, 18 H, NCCCH_3), 5.78 (s, 10 H, C_5H_5); – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 30.98$ (s, NCCCH_3), 68.84 (s, NCCCH_3), 107.95 (br, C_5H_5). – EI-MS: m/z (%) = 370 (1) $[\text{M}^+]$. – $\text{C}_{18}\text{H}_{28}\text{MoN}$ (368.4): calcd. C 58.69, H 7.66, N 7.61; found C 59.01, H 7.98, N 7.74.

Bis(tert-butylimido)bis(cyclopentadienyl)tungsten(VI) (2b): Finely powdered **1b** (384 mg, 0.90 mmol) was added to a suspension of $(\text{C}_5\text{H}_5)\text{Na}$ (87.4 mg, 0.99 mmol) in 20 mL 1,2 dimethoxyethane at -50°C . The temperature of the orange colored mixture was raised to room temperature within 30 min. and refluxed for 6 h. All volatile materials of the brown suspension were removed in vacuo and the brown, oily residue was extracted with 20 mL hexane. The evaporated hexane extract was distilled at 6×10^{-3} mbar onto a cooled finger (-30°C). The product separated as an orange-brown solid at the finger, which melted at room temperature to give a brown oil. – Yield: 252 mg (61%). – IR (film): $\tilde{\nu} = 3084$ m $\nu(\text{C-H}_{\text{ar}})$, 2986 s, 2920 s, 2896 s, 2860 s, 2804 m, 1660 sh, 1612 w $\nu(\text{C}=\text{C})$, 1448 m, 1356 m, 1288 vs and 1248 vs $\nu(\text{W}=\text{N}-\text{C})$, 1212 s, 1140 w, 1080 m, 1020 m, 960 w, 868 s and 808 vs and 740 vs $\nu(\text{C-H}_{\text{ar}})_{\text{oop}}$, 632 w, 576 w, 544 w, 472 cm^{-1} . – ^1H NMR (89.6 MHz, C_7D_8 , 360 K): $\delta = 1.15$ (s, 18 H, NCCCH_3), 5.77 (s, 10 H, C_5H_5); (89.6 MHz, C_7D_8 , 273 K): $\delta = 1.16$ (s, 18 H, NCCCH_3), 5.36 (s, 5 H, $\eta^5\text{-C}_5\text{H}_5$), 6.56 (br, 5 H, $\eta^1\text{-C}_5\text{H}_5$); (89.6 MHz, C_7D_8 , 193 K): $\delta = 1.19$ (s, 18 H, NCCCH_3), 4.69 (br, 1 H, $\eta^1\text{-H}_X$), 5.30 (s,

5 H, $\eta^5\text{-C}_5\text{H}_5$), 6.65 (br, 2 H, $\eta^1\text{-H}_{\text{B/B'}}$), 6.80 (br, 2 H, $\eta^1\text{-H}_{\text{A/A'}}$). – ^{13}C NMR (100.7 MHz, C_7D_8): δ = 31.88 (s, NCCH_3), 66.69 (s, NCCH_3), 106.90 (br, C_5H_5). – EI-MS: m/z (%) = 456 (63) [M^+], 441 (59) [$\text{M}^+ - \text{CH}_3$]. – $\text{C}_{18}\text{H}_{18}\text{N}_2\text{W}$ (456.3): calcd. C 47.38, H 6.19, N 6.14; found C 47.09, H 6.02, N 6.11.

Bis(cyclopentadienyl)bis(mesitylimido)tungsten(VI) (2c): Finely powdered **1b** (551 mg, 1.00 mmol) was added to a suspension of $(\text{C}_5\text{H}_5)\text{Na}$ (96.1 mg, 1.10 mmol) in 20 mL 1,2 dimethoxyethane at -50°C . The temperature of the red mixture was raised to room temperature within 30 min. and refluxed for 12 h. All volatile materials of the orange red suspension were removed in vacuo and the oily residue was extracted with 30 mL hexane. The extract was concentrated to approximately 8 mL. Any precipitating product was redissolved by warming the solution. Orange red crystals were isolated after one day at room temperature, and washed with 2 mL cold pentane (-70°C), and dried in vacuo. – Yield: 429 mg (74%). m.p.: 176°C . – IR (nujol): $\tilde{\nu}$ = 2986 s, 2920 s, 2896 s, 2860 s, 2804 m, 1604 w ($\text{C}=\text{C}$), 1448 m, 1356 m, 1311 s and 1281 vs ($\text{W}=\text{N}-\text{C}$), 1153 s, 1056 w, 1024 w, 1010 w, 980 w, 866 s and 810 s and 740 s ($\text{C}-\text{H}_{\text{ar}}$)_{oop}, 595 w, 582 w, 544 w, 505 w, 440 w cm^{-1} . – ^1H NMR (200.1 MHz, C_7D_8 , 375 K): δ = 2.07 (s, 6 H, $\text{Mes-}p\text{-CH}_3$), 2.19 (s, 12 H, $\text{Mes-}o\text{-CH}_3$), 5.88 (s, 10 H, C_5H_5), 6.63 (s, 4 H, Mes-H); (200.1 MHz, C_7D_8 , 310 K): δ = 2.09 (s, 6 H, $\text{Mes-}p\text{-CH}_3$), 2.19 (s, 12 H, $\text{Mes-}o\text{-CH}_3$), 5.47 (br, 5 H, C_5H_5), 6.25 (br, 5 H, C_5H_5), 6.60 (s, 4 H, Mes-H); (200.1 MHz, C_7D_8 , 193 K): δ = 2.15 (s, 6 H, $\text{Mes-}p\text{-CH}_3$), 2.24 (s, 12 H, $\text{Mes-}o\text{-CH}_3$), 5.15 (s, 1 H, $\eta^1\text{-H}_X$), 5.26 (s, 5 H, $\eta^5\text{-C}_5\text{H}_5$), 6.55 (s, 2 H, $\eta^1\text{-H}_B$), 6.57 (s, 1 H, $\eta^1\text{-H}_{B'}$), 6.71 (s, 4 H, Mes-H) 6.90 (s, 1 H, $\eta^1\text{-H}_A$), 7.01 (s, 1 H, $\eta^1\text{-H}_{A'}$). – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 19.47 (s, $\text{Mes-}o\text{-CH}_3$), 20.92 (s, $\text{Mes-}p\text{-CH}_3$), 108.40 (s, C_5H_5), 128.58 (s, Mes-C3), 131.01 (s, Mes-C2), 132.76 (s, Mes-C4), 153.71 (s, $^2J_{\text{WC}} = 32.7\text{ Hz}$, Mes-C1). – EI-MS: m/z (%) = 580 (70) [M^+], 515 (100) [$\text{M}^+ - \text{C}_5\text{H}_5$]. – $\text{C}_{28}\text{H}_{32}\text{N}_2\text{W}$ (580.4): calcd. C 57.94, H 5.56, N 4.83; found C 57.06, H 5.66, N 4.83.

Bis(tert-butylimido)dichloro(trimethylphosphane)tungsten(VI) (3): PMe_3 (100 mg, 1.31 mmol) was added to a solution of **1b** (430 mg, 1.01 mmol) in 15 mL toluene. After 2 h at room temperature, all volatile materials were removed in vacuo, and 15 mL pentane was added to the brown oily residue. Insoluble, ocher colored **3** was filtered off, washed with 5 mL pentane and was dried in vacuo. The mother liquor contained 230 mg (0.50 mmol) of slightly impure **2b**. – Yield: 201 mg (85%). – ^1H NMR (400.1 MHz, CDCl_3): δ = 1.35 (s, 18 H, NCCH_3), 1.73 (d, $^2J_{\text{PH}} = 10.4\text{ Hz}$, 9 H, PCH_3); – $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): δ = 7.55 (s, $^1J_{\text{WP}} = 363\text{ Hz}$, PCH_3); – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 16.63 (d, $^1J_{\text{PC}} = 34.5\text{ Hz}$, P-CH_3), 31.82 (d, $^4J_{\text{PC}} = 2.0\text{ Hz}$, NCCH_3), 69.61 (d, $^3J_{\text{PC}} = 2.0\text{ Hz}$, $^2J_{\text{WC}} = 26.5\text{ Hz}$, NCCH_3).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133165. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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