Section Chemical Research of the NSCS

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The Section Chemical Research (SCR) of the New Swiss Chemical Society (NSCS) has decided to publish each year in CHIMIA a collection of short papers (1–2 pages each) corresponding to the most remarkable posters or oral contributions presented at the Fall Meeting of the NSCS. The main purpose of this action is to enable the authors of the awarded contributions to develop somewhat their presentation at the Fall Meeting so as the whole readership of CHIMIA may have a chance to be aware of it. The choice of the awarded contributions is made by the Committee of the SCR which takes the responsibility for the part of subjectivity inherent in such a selection. This CHIMIA issue presents a paper pertaining to the field of inorganic chemistry, whereas those related to organic chemistry, physical chemistry and computational chemistry have already been published in the CHIMIA issue 3, p. 90–99.

The Metal Oxo [1,2]-Alkyl Shift – Towards the Aerobic Oxidation of Hydrocarbons[a])

Christian Cremer, **Heiko Jacobsen**, and **Peter Burger***

Abstract. The syntheses and X-ray crystal structures of novel monocyclopentadienyl tungsten(IV) and molybdenum(IV) complexes with additional 4,4'-disubstituted 2,2'-bipyridine ligands are presented. The preference for the observed μ-O bridged dimeric structure in the $[Cp*Mo,W(\mu\text{-}O)(4,4'\text{-}R_2\text{-bipy})]_2^{2+}$ compounds rather than a monomeric structure with a terminal M=O unit is rationalized by Extended *Hückel* MO calculations. In addition, a synthetic route to C_1-, C_2- and Si-bridged *ansa*-magnesocenes is described and X-ray crystal structures of representative examples displaying an unsymmetrical cyclopentadienyl binding mode are provided. The *ansa*-magnesocenes are excellent starting materials for the syntheses of bridged dicyclopentadienyl ditungsten complexes with W,W multiple bonds. The X-ray crystal structure of the C_1-bridged tetrakis-dimethylamide compound, $Me_2C[(\eta^5\text{-}C_5H_4)W(NMe_2)_2)]_2$, is presented.

Correspondence: Dr. P. Burger
Anorganisch-Chemisches Institut
Universität Zürich
Winterthurerstrasse 190
CH–8057 Zürich

Introduction and Background

Chemistry in our group is directed towards the development of new methods for the *aerobic* oxidation of organic substrates with an emphasis on alkane functionalization, *e.g.*, the oxidation of CH_4 to CH_3OH. Mechanistically, this requires quite a number of very challenging steps, such as O_2 and C–H bond cleavage, C–O bond formation *etc.* The focus of our current investigations is the development of the *thermal non-radical* oxygen transfer step shown below:

$$[M]\!\!=\!\!O \longrightarrow [M]\!-\!O\!-\!R$$

So far, however, still very little is known about the R–M=O [1,2]-shift [1]; it deserves special mentioning that *Sharpless* and coworkers have included this step in their mechanistic scheme for the enantioselective *cis*-hydroxylation process of olefins using OsO_4/chiral amine ligands [2].

Poster Presentations

One of our target systems, the novel mononuclear cyclopentadienyl tungsten-(IV) oxo methyl complex Me–[W]=O is shown in *Fig. 1*.

The 4,4'-disubstituted 2,2'-bipyridine (bipy) ligands in these complexes cover a wide range of σ(*Hammett*) parameters and have been chosen to examine exclusively the electronic nature of the [1,2]-shift. The synthetic access to this type of W^{IV} compound was sought *via* the hitherto unknown tungsten(IV) complex, $(Cp*WCl_3)_2$. This extremely air-sensitive paramagnetic complex was obtained by one electron Na/Hg reduction of $Cp*WCl_4$; its dimeric structure was confirmed by single crystal X-ray diffraction (*Fig. 2*).

The puckered arrangement of the $W_2(\mu$-$Cl)_2$ unit in the $(Cp^*WCl_3)_2$ syn-dimer enables a bonding metal-metal interaction – the observed W–W distance of 305.3(1) pm is in the range of W–W single bonds. The dimer is an excellent starting material for the synthesis of $Cp^*WCl_3(4,4'$-R_2-bipy), i.e., upon addition of the 2,2'-bipyridine ligands facile cleavage of the dimer occurs and the weakly paramagnetic, pseudo-octahedral 4,4'-R_2-bipy complexes are obtained in good to excellent yields. Weakening of the W–Cl bonds in the latter electron rich compounds is indicated through the observation of elongated W–Cl bonds (avg. 250 pm) in the X-ray crystal structure of the methyl derivative, $Cp^*WCl_3(4,4'$-Me_2-bipy). This is further corroborated by conductivity measurements in solution and through the formation of the cationic 16-electron species, $[WCl_2Cp^*(4,4'$-Me_2-bipy)]$^+$, upon halide abstraction. The introduction of the oxygen ligand is straightforward by hydrolysis in deoxygenated H_2O, and, upon salt exchange with PF_6^- or SbF_6^- the dimeric $(\mu$-$O)_2$-bridged dicationic complexes are obtained in excellent yields. The X-ray crystal structure of the dark-blue, highly coloured ($\varepsilon \approx 10^4$ l·mol^{-1}·cm^{-1}) methyl derivative (Me_2-bipy) (Fig. 3) confirmed the dimeric structure and based on the W–W distance of 273.2(1) pm and electron counting arguments, a W=W bond is proposed.

The formation of dimers puzzled us for a while since the analogous Mo phosphine complex with the small PMe_3 ligand, $[MoCp(PMe_3)_2(=O)]^+$, has been reported earlier by Green et al. to be monomeric both in solution and in the solid state [3]. Initially, we anticipated steric arguments would explain this apparent difference. However, since we could show that the analogous tungsten complex with the bulky 4,4'-(t-Bu)$_2$-2,2'-bipyridine ligand is also dimeric, it was deemed that electronic factors are determining the dimer formation. To rule out that the formation of the dimers is due to a stronger metal–metal bond in the ditungsten complexes, we have also prepared and crystallographically characterized the corresponding Mo complex, $[MoCp^*(\mu$-$O)(4,4'$-Me_2-bipy)]$_2^{2+}$. Its dimeric structure could unambiguously be demonstrated in the solid state by X-ray crystallography and in solution by UV/VIS- and IR-spectroscopy. This suggested that other/additional factors are operative leading to a preference for the observed μ-O-bridged complex rather than a monomeric structure with a terminal M=O unit, i.e., $[Cp^*Mo,W(=O)(4,4'$-Me_2-bipy)]$^+$.
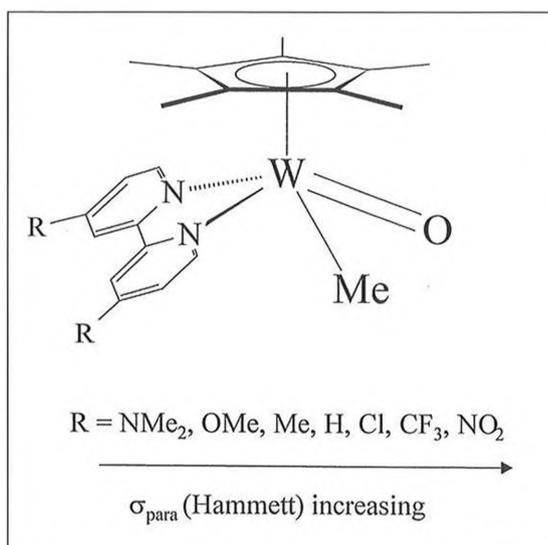

Fig. 1. $[W(=O)Cp^*(Me)(4,4'$-R_2-2,2'-bipyridine)]$ system

$R = NMe_2$, OMe, Me, H, Cl, CF_3, NO_2

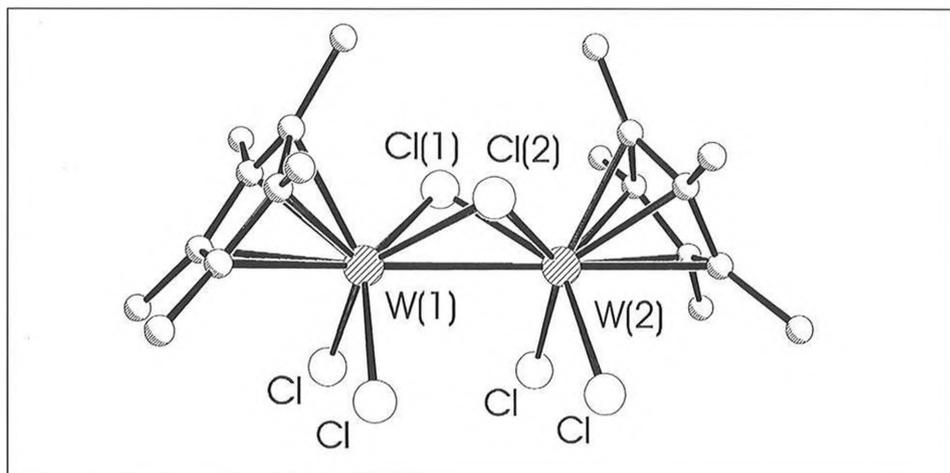σ_{para} (Hammett) increasing

Fig. 2. X-Ray crystal structure of dimeric $[WCp^*Cl_3]_2$
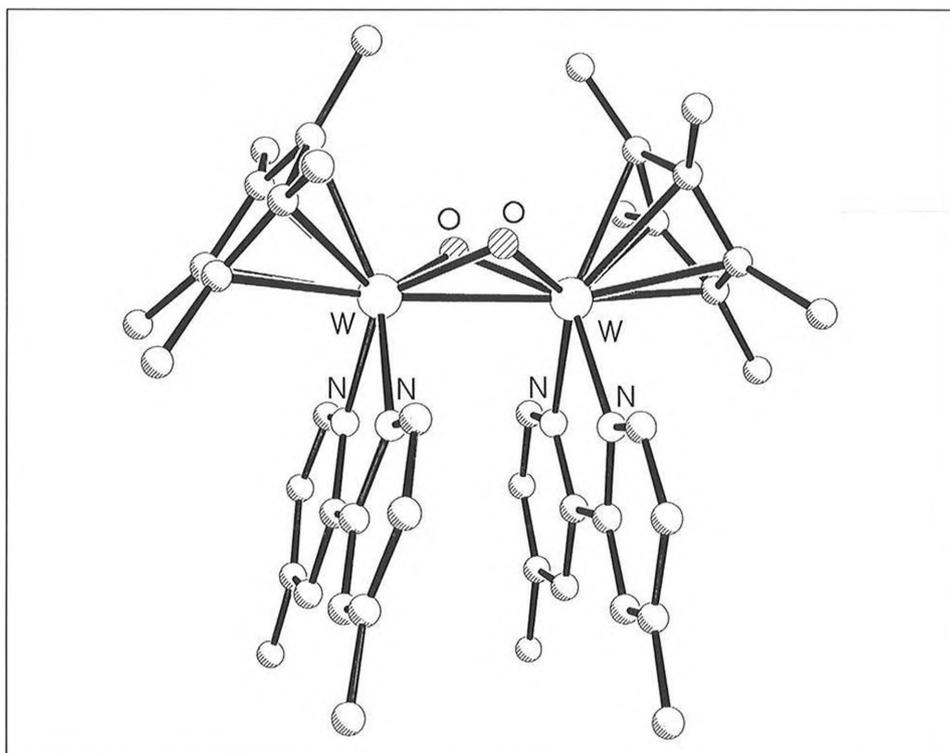

Fig. 3. X-Ray crystal structure of $[W(\mu$-$O)Cp^*(4,4'$-Me_2-bipy)]$_2^{2+}$. The anions are not shown.

Finally, we turned to extended *Hückel* (EHT) calculations to investigate differences in the electronic structures of the phosphine and bipy compounds. These were performed for the hypothetical monomeric model complexes, [W(=O)Cp(PH$_3$)$_2$]$^+$ and [W(=O)Cp(HN=CH–CH=NH)]$^+$, in idealized C_s symmetry with the diimine (HN=CH–CH=NH) and the PH$_3$ ligand representing the bipy and the PMe$_3$ donors, respectively. The inspection of the frontier orbitals in both complexes provided a nice rationale for the observed structural difference in the N- and P-donor substituted complexes (*Fig. 4*).

Although the MOs have apparently a great resemblance in both model compounds, there is a major difference between the diimine and the PH$_3$ ligand substituted complexes. It can be immediately recognized from *Fig. 4* that the HOMO and LUMO are *inverted* in the N- and P-donor compounds. In the N-donor complex the LUMO is essentially a W-centered d$_z^2$ orbital which is perfectly suited as an *acceptor* MO for donation from the oxygen n-orbitals to form the observed dimeric complex. On the contrary, the d$_z^2$ orbital in the phosphine compound is *filled* (HOMO). It is, therefore, no longer available as an acceptor MO thus providing an explanation why these molecules prefer to be monomeric.

Since this unique orbital is essentially a non-bonding metal based d$_z^2$ orbital, its energy is (as expected) independent from the type of donor ligand (*cf. Fig. 4*). Hence, the inversion of the HOMO/LUMO in the two related systems has to be associated with the other sets of orbitals shown in *Fig. 4*. Inspection of the latter orbitals, the HOMO in the N-donor and the LUMO in the phosphine complex, reveals that they are π*-antibonding with respect to the W=O unit in both molecules. In the diimine complex, however, π-back donation to the low lying π* orbital of the N-donor ligand gives rise to an overall lowering of the energy. In the phosphine substituted complex on the other hand, there is no interaction of this type and therefore the d$_z^2$ W-centered orbital becomes the HOMO.

From this picture it becomes evident that the extent of π-back donation has a strong influence on the ordering of the frontier orbitals. This suggests that one might also be able to obtain monomeric complexes for the N-donor compounds with poor π-acceptor bipy ligands, *e.g.*, 4,4'-(NMe$_2$)$_2$-bipy. We are currently in the process of obtaining experimental support for this idea – the latter ligand system would also allow to perform a nice additional check: For the corresponding complex with the protonated 4,4'-(NHMe$_2^+$)$_2$-bipy ligand once again a dimeric structure, *i.e.* [W(μ-O)Cp*(4,4'-(NHMe$_2^+$)$_2$-bipy)]$_2^{2+}$, would be expected due to the enhanced π-accepting power of the protonated N-donor.

In an additional poster presentation, we have described the syntheses and X-ray crystal structures of metal–metal multiple bonded dinuclear complexes, [M]≡[M]. Still within the framework of non-radical oxidations, research in this area is inspired by the idea that the metal-metal multiple bond in these compounds might serve for 'clean' O$_2$ activation and lead to facile formation of two [M]=O units. Shown below is the synthesis and X-ray crystal structure of one representative example, the novel C$_1$-bridged dicyclopentadienyl tetrakis-dimethylamide ditungsten complex (*Fig. 5*).

Although the synthesis of the related unbridged cyclopentadienyl complexes had been described earlier by *Chisholm* and coworkers [4], our initial attempts to obtain bridged W≡W bonded ditungsten complexes using the rather insoluble lithiated Cp reagents, (Cp$_2$X)Li$_2$ (X = CMe$_2$, SiMe$_2$) had only been of very limited success. Since this was attributed to the formation of cyclopentadienyl bridged oligomers, well-defined, soluble Cp transfer reagents were sought to apply the dilution principle. As shown in *Fig. 5* (top trace) use of the novel, soluble *ansa*-magnesocenes, for which a new route was
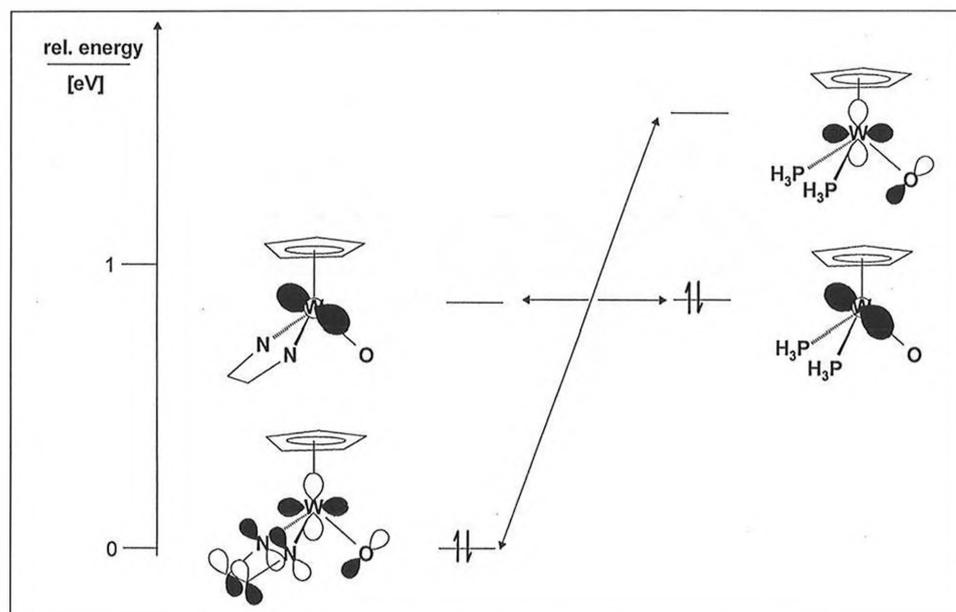

Fig. 4. *HOMO and LUMO for L$_2$ = diimine (left) and L$_2$ = (PH$_3$)$_2$ (right) for C$_s$-symmetrical CpWL$_2$(=O)$^+$ model systems*
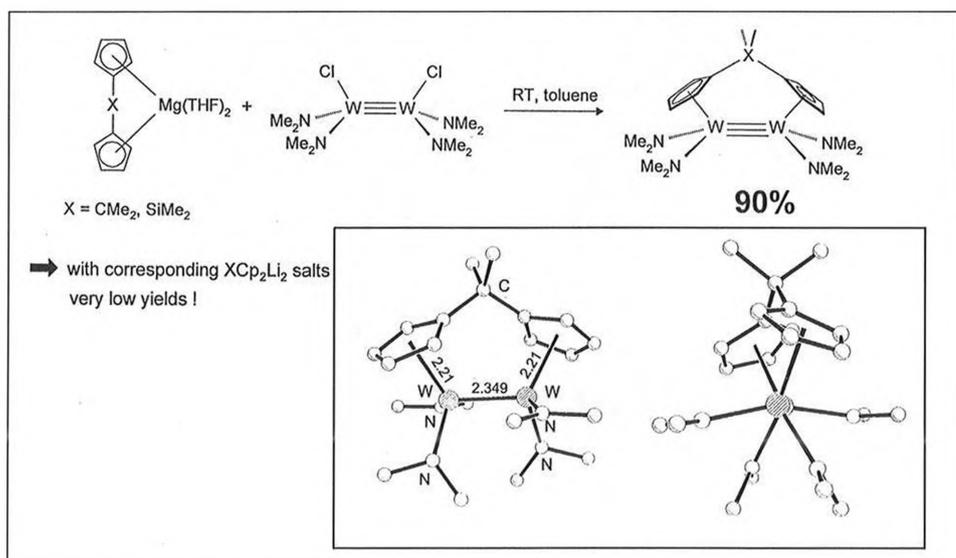

Fig. 5. *Synthesis and X-ray crystal structure of the bridged dicyclopentadienyl ditungsten metal-metal multiple bonded complex* (selected distances are given)
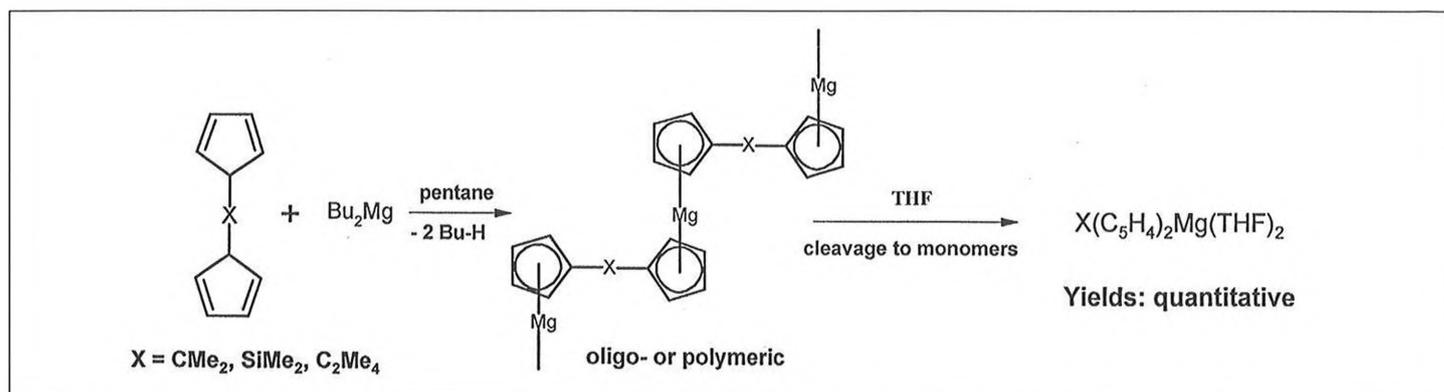
Fig. 6. *Syntheses of* ansa-*magnesocenes*

developed (*Fig. 6*) indeed gave the desired ditungsten complexes in excellent yields.

With this, a complete new research area was opened that led eventually to the discovery of the unusual cyclopentadienyl coordination mode in the bridged magnesocenes. This is best presented by the X-ray crystal structure of the C_1-bridged *ansa*-magnesocene · 2 THF shown below (*Fig. 7*).

We have now quite a number of further examples for the unsymmetrical binding of cyclopentadienyl ligands in bridged $X(Cp_2)Mg(L)_2$ complexes with $X = CMe_2$, C_2Me_4, $SiMe_2$ and $L = \sigma$-donor. Very recently, we even were able to isolate an exciting analogue of the Mg complex with the weak methyl isonitrile donor, for which we had expected *some* stability based on prior density functional theory (DFT) calculations. The X-ray crystal structure of this compound is shown in *Fig. 8*.

In solution, these molecules are highly fluxional and evidence for ligand dissociation processes from $XCp_2Mg(L_2)$ with concomitant formation of $XCp_2Mg(L)$ and XCp_2Mg has been provided by VT NMR-studies.

[1] S.N. Brown, J.M. Mayer, *J. Am. Chem. Soc.* **1994**, *116*, 2219.
[2] D.J. Berrisford, C. Bolm, K.B. Sharpless, *Angew. Chem.* **1995**, *107*, 1159.
[3] P.D. Grebenik, M.L.H. Green, A. Izquierdo, V.S.B. Mtetwa, K. Prout, *J. Chem. Soc., Dalton Trans.* **1987**, 9.
[4] M.H. Chisholm, M.J. Hampden-Smith, J.C. Huffman, J.D. Martin, K.A. Stahl, K.G. Moodley, *Polyhedron* **1988**, 7, 1991.
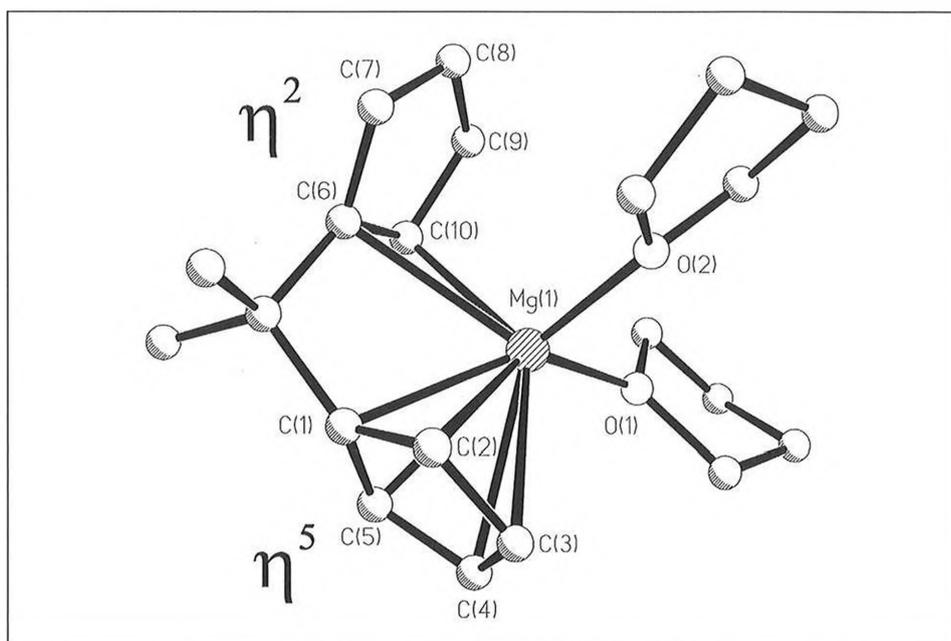
Fig. 8. *X-Ray crystal structure of the first Mg isonitrile complex,* $Me_2C(C_5H_4)Mg$ (THF)(CNMe) (selected distances are given)
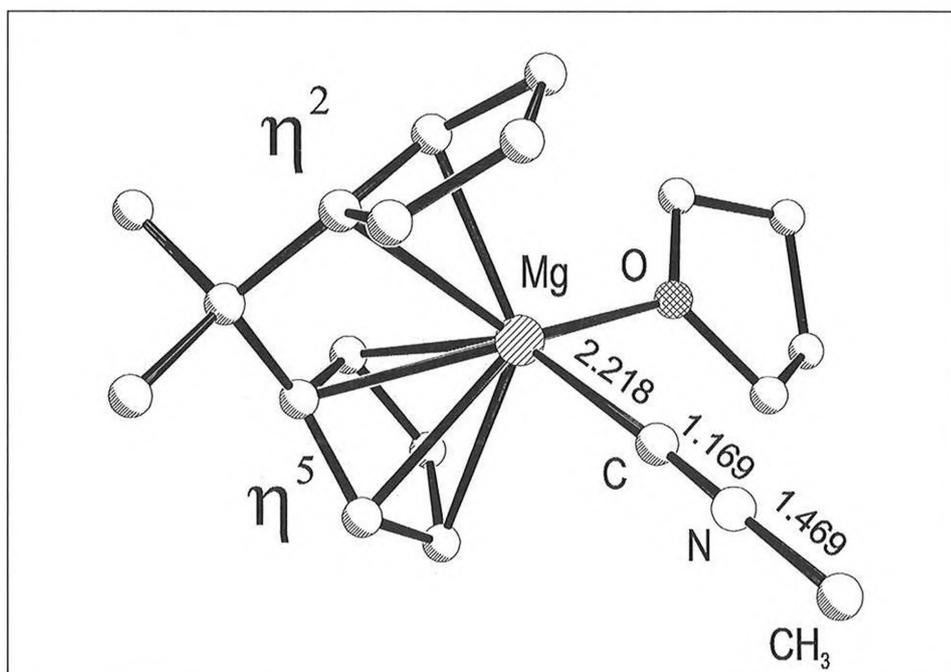
Fig. 7. *X-Ray crystal structure of* $Me_2C(C_5H_4)Mg$ · 2 THF