

(α -Triphenylphosphonio)methylidene Imido Complexes of Molybdenum, Tungsten and Rhenium: the First Complexes Exhibiting Metal–Ligand Multiple-bonding with Two Carbon as well as Two Nitrogen Centres

Jörg Sundermeyer,* Klaus Weber and Oliver Nürnberg

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, 8700 Würzburg, Germany

The synthesis of tetrahedral complexes $[\text{Mo}(\text{NBu}^t)_2(\text{CHPPh}_3)_2]$, $[\text{W}(\text{NBu}^t)_2(\text{CHPPh}_3)_2]$ and $[\text{Re}(\text{NBu}^t)_3(\text{CHPPh}_3)]$ having four π -donor ligands is reported; the X-ray structure of $[\text{W}(\text{NBu}^t)_2(\text{CHPPh}_3)_2]$ reveals strong π -interactions of both imido ligands $[\text{=NBu}^t]$ as well as (α -triphenylphosphonio)methylidene functions $[\text{=CHPPh}_3^+]$, with the d^0 metal centre.

Organo diimido complexes of the type $[\text{M}(\text{NR})_2\text{R}_2]$ ($\text{M} = \text{Mo}, \text{W}$) have recently been the focus of considerable interest. Complexes of this class were first reported by Nugent *et al.* who isolated dimeric methyl derivatives $[\text{M}(\text{NBu}^t)(\mu\text{-NBu}^t)\text{Me}_2]_2$ ($\text{M} = \text{Mo}, \text{W}$)¹ exhibiting unsymmetrically bridging imido ligands. Wilkinson *et al.* showed that by introducing sterically demanding mesityl groups these complexes become monomeric² and, that the strong π -donor

capability of the imido ligand allows the synthesis of the related complex $[\text{Cr}(\text{NBu}^t)_2(\text{mesityl})_2]$, the first known organyl of chromium(vi).³ More recently, the synthetic value of dineopentyl derivatives and other non β -H containing alkyls was discovered by the groups of Schrock and Osborn.⁴ The latter complexes may serve as key compounds for the preparation of metathetically active alkylidene imido species.

Our interest in this chemistry originated from the fact that

there are no reports on (α -phosphonio)alkylidene imido complexes. This is surprising because alkylidene imido chemistry is developing rapidly^{4,5} and complexes of the type $[M=CH-PR_3^+]$ are isoelectronic with typical alkylidene complexes of the Schrock-type $[M=CH-SiR_3]$. In fact, phosphorus ylide chemistry has not been systematically extended to higher-valent oxo and especially imido complexes of the early transition metals so far.⁶ The mechanism of the low yield formation of $[MoO_2(\text{mesityl})C(\text{mesityl})PBU^n_3]$, the only reported (α -phosphonio)alkylidene oxo complex, has remained speculative.^{6a}

We have found that the transylidation reaction of $[Mo-(NBu^t)_2Cl_2]^{4a}$ or $[W(NBu^t)_2Cl_2(py)_2]$ with four equivalents of methylenetriphenylphosphorane affords the highly reactive title complexes $[Mo(NBu^t)_2(CHPPH_3)_2]$ **3a** and $[W(NBu^t)_2(CHPPH_3)_2]$ **3b** in excellent yield. This was surprising because phosphorus ylides are known to be very susceptible to oxidation by electron deficient metal complexes.⁸ In both starting complexes the imido ligands are masking the formally highest oxidation state of the metal centre by acting as strong π -donor ligands. Therefore, no redox behaviour was observed and we were able to isolate and fully characterise all intermediates in this multistep reaction. It proceeds *via* the pentacoordinate classical ylide complexes **1a,b** which are isolated when the parent compounds are treated with one equivalent of $Ph_3P=CH_2$ in toluene. In these complexes the α - CH_2 protons are acidic. The corresponding carbanion is stabilised by the σ, π -acidic metal fragment as well as the negative hyperconjugative effect of the α -triphenylphosphonio substituent.⁹ Addition of a second equivalent of the base $Ph_3P=CH_2$ leads to precipitation of $[Ph_3PMe]Cl$ and formation of the metal substituted phosphorus ylides **2a,b**[†] which themselves may act as precursors for the preparation of the title complexes **3a,b**.

The structure of **3b**, as determined by X-ray diffraction, is shown in Fig. 1.[‡] The compound is a tetrahedral monomer in

the solid state consistent with the spectroscopic data.[§] Both W–C bond distances [2.043(3) and 2.051(3) Å] fall into the upper range acceptable for double bonds.^{10a} The corresponding W–C distances in $[W(NBu^t)(\mu-NBu^t)Me_2]_2$ are 2.171(5)

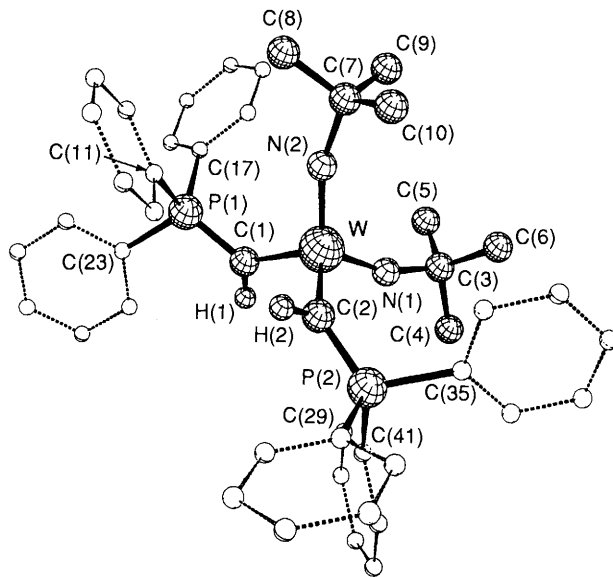


Fig. 1 Molecular structure of $[W(NBu^t)_2(CHPPH_3)_2]$ **3b** (SCHAKAL plot). Hydrogen atoms other than H(1) and H(2) are omitted and phenyl carbon atoms are reduced in size for clarity. Selected bond lengths (Å) and angles ($^\circ$) as follows: W–N(1) 1.773(3), W–N(2) 1.771(3), W–C(1) 2.051(3), W–C(2) 2.043(3), P(1)–C(1) 1.682(3), P(1)–C(11) 1.817(3), P(1)–C(17) 1.828(3), P(1)–C(23) 1.821(3), P(2)–C(2) 1.676(3), P(2)–C(29) 1.824(3), P(2)–C(35) 1.827(4), P(2)–C(41) 1.828(3), N(1)–C(3) 1.439(4), N(2)–C(7) 1.441(4); N(1)–W–N(2) 116.5(1), N(1)–W–C(1) 108.3(1), N(2)–W–C(1) 108.8(1), C(1)–W–C(2) 109.3(1), W–N(1)–C(3) 160.7(2), W–N(2)–C(7) 161.7(2), W–C(1)–P(1) 127.6(2), W–C(2)–P(2) 131.3(2), C(1)–P(1)–C(11) 112.3(2), C(1)–P(1)–C(17) 116.7(2), C(2)–P(2)–C(29) 110.1(2), C(2)–P(2)–C(41) 117.5(2), torsion angles: P(2)–C(2)–W–N(1) 4.25, P(1)–C(1)–W–N(2) 8.47, dihedral angle of the planes $[W, C(1), P(1)]$ and $[W, C(2), P(2)]$: 99.68.

[†] In **2a,b**, the barrier to rotation about the metal–carbon double bond of the alkylidene ligands has been determined by observing coalescence of both imido signals in the 90 MHz 1H NMR spectra: **2a**: $\Delta G^\ddagger_{268 K} = 13.1$ kcal mol⁻¹; **2b**: $\Delta G^\ddagger_{265 K} = 12.9$ kcal mol⁻¹ (1 cal = 4.184 J). The latter values as well as the value of the corresponding chromium complex $[Cr(NBu^t)_2(CHPPH_3)Cl]^{15}$: $\Delta G^\ddagger_{363 K} = 17.9$ kcal mol⁻¹ lie within the typical range for alkylidene complexes of the Schrock-type; for a review see: R. R. Schrock, W. E. Crowe, G. C. Bazan, M. DiMare, M. B. O'Regan and M. H. Schofield, *Organometallics* 1991, **10**, 1832.

[‡] *Crystal data for 3b*: $C_{46}H_{50}N_2P_2W \cdot 1.5 C_6D_6$, $M = 876.72$ g mol⁻¹ (1002.82 g mol⁻¹ incl. C_6D_6), triclinic, $P\bar{1}$ (No. 2), $a = 12.902(1)$, $b = 13.273(2)$, $c = 17.109(1)$ Å, $\alpha = 107.35(1)$, $\beta = 97.96(1)$, $\gamma = 114.02(1)^\circ$, $Z = 2$, $V = 2439.3$ Å³, $D_c = 1.37$ g cm⁻³, $\mu = 25.1$ cm⁻¹, intensity measurement: Enraf-Nonius CAD4-diffractometer with Zr-filtered Mo-K α -radiation ($\lambda = 0.70930$ Å) at $T = 241$ K, crystal $0.7 \times 0.5 \times 0.4$ mm, $\omega/2\theta$ -scan, $2\theta_{max} = 44^\circ$, 6264 reflections measured, 5936 unique, 5499 observed [$F_o > 3\sigma(F_o)$], Lp-correction and empiric absorption correction, minimum transmission 82.2%, structure solution with direct methods (SHELXS-86) and refinement with least-squares (Enraf-Nonius SDP), 546 parameter, $R = 0.021$, $R_w = 0.025$, residual electron density $+0.65/-0.74$ e Å⁻³. The crystal was mounted in a glass capillary under an atmosphere of argon. During structure solution it turned out, that 1.5 molecules of C_6D_6 are present in one asymmetric unit. The two hydrogen atoms at the α -C-atoms [H(1) and H(2)] have been localized in a difference-Fourier analysis, and could be refined isotropically. The positions of all other H-atoms were calculated according to ideal geometry ($d_{C-H} = 0.95$ Å) and were included in the structure-factor calculation in the last cycles of FMLS refinement. The two largest peaks in the final difference-Fourier analysis lie at a distance of 1.02 and 1.08 Å from the W-atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] Satisfactory analyses have been obtained for all new compounds described.

Selected spectroscopic data: 1H and $^{13}C\{^1H\}$ NMR data are recorded at 25 °C unless otherwise stated and given as δ relative to SiMe₄, multiplicity, coupling constant J in Hz and assignment; ^{31}P NMR data: H_3PO_4 external standard.

2a: 1H (90 MHz, $[^2H_8]$ toluene, 60 °C): 1.29 (s, 18 H, CM_e_3), 8.04 (d, $J_{P,H}$ 0.6, 1 H, MoCHP), 7.00–7.06 and 7.55–7.65 (m, 15 H, C_6H_5); ^{13}C (101 MHz, C_6D_6): 32.44 (s, CM_e_3), 67.70 (s, CM_e_3), 127.75 (d, $J_{P,C}$ 48.8 MoCHP); ^{31}P (36 MHz, C_6D_6): 24.92; IR (Nujol): $\nu(Mo=N-C)$ 1242, 1203, $\nu(P-C)$ 906.

2b: 1H (400 MHz, $[^2H_8]$ toluene, 80 °C): 1.22 (s, 18 H, CM_e_3), 6.14 (d, $J_{P,H}$ 1.6, $J_{W,H}$ 10.7 satellites, 1 H, WCHP), 6.98–7.09 and 7.53–7.60 (m, 15 H, C_6H_5); ^{13}C (101 MHz, C_6D_6): 33.97 (s, CM_e_3), 66.26 (s, $J_{W,C}$ 25.9, CM_e_3), 118.19 (d, $J_{P,C}$ 57.1, $J_{W,C}$ 171.5, WCHP); ^{31}P (36 MHz, C_6D_6): 30.50 (s, $J_{W,P}$ 36.6); IR (Nujol): $\nu(W=N-C)$ 1272, 1236, $\nu(P-C)$ 910.

3a: 1H (200 MHz, C_6D_6): 1.28 (s, 18 H, CM_e_3), 4.62 (d, $J_{P,H}$ 2.3, 2 H, MoCHP), 7.05–7.10 and 7.88–7.98 (m, 30 H, C_6H_5); ^{13}C (101 MHz, C_6D_6): 33.17 (s, CM_e_3), 65.48 (s, CM_e_3), 73.61 (d, $J_{P,C}$ 54.0, MoCHP); ^{31}P (36 MHz, C_6D_6): 21.82; IR (Nujol): $\nu(Mo=N-C)$ 1252, 1220, $\nu(P-C)$ 908.

3b: 1H (400 MHz, C_6D_6): 1.30 (s, 18 H, CM_e_3), 3.81 (d, $J_{P,H}$ 0.5, $J_{W,H}$ 8.7, 2 H, WCHP), 7.06–7.10 and 7.88–7.97 (m, 30 H, C_6H_5); ^{13}C (101 MHz, C_6D_6): 33.92 (s, CM_e_3), 65.40 (s, $J_{W,C}$ 29.2, CM_e_3), 76.99 (d, $J_{P,C}$ 61.8, $J_{W,C}$ 149.6, WCHP); ^{31}P (161 MHz, C_6D_6): 27.51 (s, $J_{W,P}$ 32.2); IR (Nujol): $\nu(W=N-C)$ 1284, 1240, $\nu(P-C)$ 912.

4: 1H (400 MHz, C_6D_6): 1.39 (s, 27 H, CM_e_3), 3.14 (d, $J_{P,H}$ 5.3, 1 H, ReCHP), 7.00–7.10 and 7.73–7.81 (m, 15 H, C_6H_5); ^{13}C (101 MHz, C_6D_6): 32.10 (s, CM_e_3), 35.81 (d, $J_{P,C}$ 85.1, ReCHP), 66.76 (s, CM_e_3); ^{31}P (161 MHz, C_6D_6): 24.49; IR (Nujol): $\nu(Re=N-C)$ 1261, 1207, $\nu(P-C)$ 938.

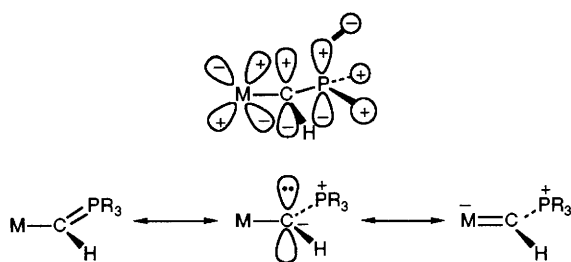


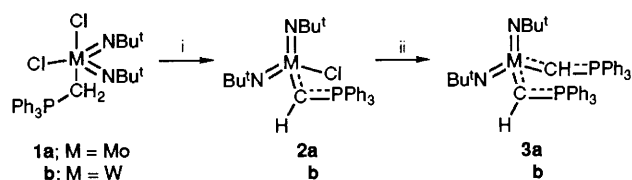
Fig. 2 Bonding situation and resonance formulae illustrating the competitive π -interaction of empty metal d-orbitals and the π^* -orbital of the R_3P -substituent with the lone pair at the sp^2 -carbon centre

and 2.163(6) Å.¹ Taking the complex $[W(CBu^t)(CHBu^t)-(CH_2Bu^t)(dmpe)]$ for comparison [$W=C$: 1.942(9) and $W-C$: 2.258(8) Å],¹¹ we have to consider at least a significant $W-C$ double bond character in **3b**. The positions of the α -CH protons could be refined isotropically. Both carbanionic centres C(1) and C(2) are trigonal-planar (sum of angles 359 and 361°). The lone pairs at the α -C(sp^2) atoms are facing a competitive situation of π -bonding with empty metal d-orbitals and with σ^*, π^* -molecular orbitals of the triphenylphosphonio substituent (negative hyperconjugation).⁹ The influence of this interaction is reflected in the relatively short α -C-P bond lengths [1.682(3) and 1.676(3) Å] compared with the other C_{ar} -P bond distances [average: ca. 1.824 Å].

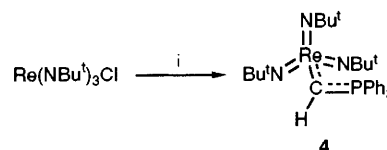
In a tetrahedral d^0 complex up to five π -interactions with p-orbitals of the four donor ligands are possible.^{10b} The two strongest π -bonds are made by the lower e set of metal orbitals. The upper t_2 orbitals are involved in bonds of both σ - and π -symmetry. Owing to their overlap population, the latter are less effective in π -bonding and are believed to contribute the equivalent of one effective π -bond altogether.^{10b,12} As a consequence of four competing strong π -donor ligands for empty metal d-orbitals, the complexes **3a,b** are electronically more saturated than the related dimethyl derivatives, the $W-N$ bond distances [1.773(3) and 1.771(3) Å] are relatively long and the corresponding bond angles $W-N-C$ [160.7(2) and 161.7(2)°] belong to the lowest observed for tungsten diimido complexes.^{10c} Both (α -phosphonio)methylidene ligands adopt a staggered geometry, which allows a maximum of π -bonding for both carbon centred lone pairs. On the other hand, both of the triphenylphosphonio substituents adopt a *syn*-periplanar conformation with respect to one of the two imido ligands, the lone pair of the corresponding bent imido moiety pointing towards the positively charged phosphonio group. A similar stereoelectronic preference¹³ was observed in the neopentylidene imido complex $[W(CHBu^t)(N-2,6-C_6H_3-Pr^i)_2(OBu^t)_2]$.^{4b}

The imido rhenium chloride $[Re(NBu^t)_3Cl]$ ¹⁴ follows a similar pattern of reactivity, but by using the triphenylsubstituted methylenephosphorane (1 equiv.), we were not able to isolate an intermediate ylide complex. The α -H deprotonation step seems to be much faster than the initial nucleophilic attack. Reaction with two equivalents of ylide gave a near to quantitative yield of the related (α -triphenylphosphonio)methylidene rhenium complex **4**.

Consistent with the ¹³C and ¹H NMR spectroscopic data the metal-tuned phosphorus ylides **2a,b** and **3a,b** and **4** show an enhanced carbon nucleophilicity compared with alkylidene complexes of the Schrock-type, which can be of synthetic value in C-C bond formation and C-O bond cleavage reactions.¹⁵ We hope, that compounds having more polar metal carbon π -bonds may also be valuable precursors for catalytically active complexes in olefin metathesis. We have, therefore, extended the reaction pattern described here to related alkyl substituted methylenephosphoranes and isolobal d^0 imido complexes of niobium, tantalum and chromium.¹⁵



Scheme 1 Reagents and conditions: i $Ph_3P=CH_2$ (1 equiv.) in toluene, yield 85–95%, ii $Ph_3P=CH_2$ (2 equiv.) in toluene, yield 90–95%



Scheme 2 Reagents and conditions: i $Ph_3P=CH_2$ (2 equiv.) in toluene, yield 90%

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