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Preliminary Communication

Unexpected ring-expansion of "axially prostereogenic" biaryl lactones by methylenephosphoranyl-substituted imido complexes of molybdenum and tungsten *,**

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Abstract

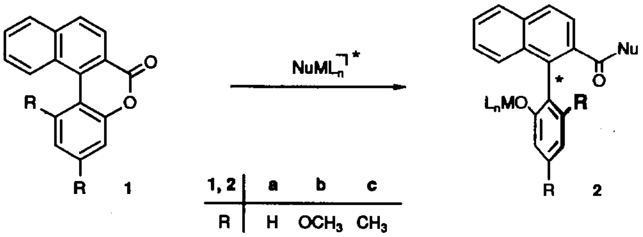
Transition-metal-substituted phosphorus ylides $M(N^tBu)_2(CH{=}PPh_3)Cl$, with M = Mo, W, have been shown to be useful *C*-nucleophiles for the selective C–O bond cleavage of benzocoumarin-type "axially prostereogenic" biaryl lactones. The reaction of the metallo-ylide with the lactone leads to an eight-membered metallacycle as established by spectroscopic data and confirmed by an X-ray diffraction study of one of the products.

Biaryl lactones of the general type **1** [3,4] are useful precursors for the stereoselective formation of axially chiral biaryl compounds **2** [5]. The lactones **1** have drastically lowered atropisomerization barriers compared with the final non-bridged biaryls [6], but can very efficiently be transformed into the configuratively-stable biaryls **2** by highly diastereo- or enantio-selective ring-opening reactions involving chiral metallated nucleophiles (see Scheme 1) [7–10].

Although investigations aimed at Lewis acid assisted ring-opening reactions have only recently begun [11], chiral metallated (*i.e.* formally anionic) *O*-, *N*-, or *H*-nucleophiles have already been found to deliver high atropisomer-selectivities in this remarkable type of stereo-controlled reaction. In contrast, ring-opening reactions with chiral *C*-nucleophiles, for which an asymmetric induction at the axis with simultaneous carbon framework enlargement of the molecule had been expected, gave no detectable atropisomeric excess [6], probably because of the configurative instability of the resulting (or intermediate) ketones **3**, by a ring-closure/ring-opening mechanism *via* rapidly helimerizing metallated lactolates **4** (*cf.* Scheme 2) [6].

A promising new class of interesting carbon nucleophiles is represented by the methylenephosphoranyl substituted imido complexes $M(N^tBu)_2\ (CH{=}PPh_3)Cl$ for M = Mo (**7**), W (**8**), which can be readily obtained by transylidation of the corresponding diimidodichlorides $M(NR)_2Cl_2$ (**5**) or their pyridine complexes **6** with two equivalents of triphenylmethylenephosphorane $Ph_3P{=}CH_2$ (Scheme 3) [2].

A characteristic feature of these complexes is the low coordination number at the metal center and the d^0 electronic configuration of the σ,π-acidic metal fragment $M' = [M(N^tBu)_2Cl]^+$, which is responsible for a substantial degree of $p_\pi \rightarrow d_\pi$ interaction and M–C double-bond character. The resonance forms **A–C** provide the best description of the bonding situation within the M–C–P moiety (*cf.* Scheme 3) [2,12]. The most extensive study of the reactions of similar transition-metal-substituted phosphorus ylides with organic carbonyl compounds was made with Group IV metallocene derivatives of the type $Cp_2M(CH{=}PPh_3)R$ [13*]. Despite of their lower ylide nucleophilicity, these com-



* : Stereogenic unit (stereocenter or -axis)

Scheme 1. The directed, atroisomer-selective, ring-opening of "axially prostereogenic" biaryl lactones.

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* Novel concepts in directed biaryl synthesis, Part XVIII; for Part XVII, see ref. 1.

** Highervalent derivatives of the d-metal acids, Part V; for Part IV, see ref. 2.

* Reference number with asterisk indicates a note in the list of references.

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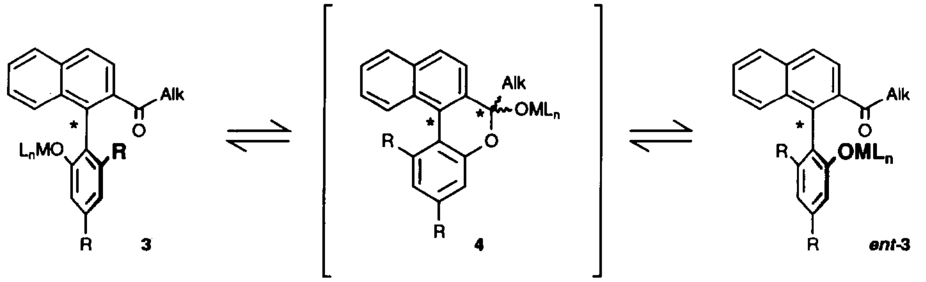


Scheme 2. Possible helimerization mechanism of the biaryl phenolate/ketones **3**, *via* configuratively unstable cyclic lactolates **4**.

plexes exhibit Wittig-type reactivity. In the reactions enolizable ketones give the expected olefins, leaving enolate complexes as the only metal-containing species, but the non-enolizable ketone $Ph_2C{=}O$ gives $Ph_3P{=}O$, $Ph_2C{=}CH_2$ and an insertion product of $Ph_2C{=}O$ into the adjacent M–C (sp^3) bond.

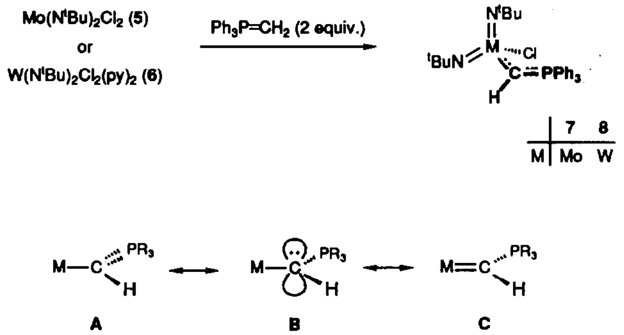
In view of the interesting properties of metal-tuned phosphorus ylides, we decided to seek to take advantage of our reagents **7** and **8** as potential *C*-nucleophiles for the directed ring-opening reaction of "axially prostereogenic" lactones **1**. Surprisingly the reaction at 60°C in benzene yielded only a single product, which was obtained in a nearly quantitative yield [14*].

^1H NMR spectroscopy indicated that the product contains both the complete molecular skeleton of the lactone moiety *and* the metal complex unit. In view of the high-field shift of the signal from the substituent R next to the biaryl axis of the organic substrate [for **9b** ($R = OCH_3$, M = Mo) $\delta = 3.11$ ppm, compared with 3.81 ppm in the starting material **1b**], it can be concluded that the two aromatic moieties are located in more orthogonal position towards each other, showing that the lactone ring has apparently been cleaved.

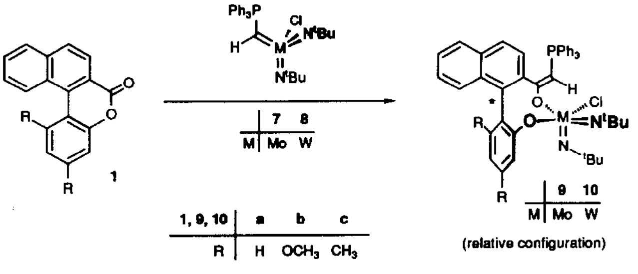
A ^{13}C NMR resonance at 190 ppm, *i.e.* in the carbonyl region, could not be attributed to a typical C=O double bond because of the lack of a corresponding absorption in the IR spectrum. The inequivalence of the ^1H and ^{13}C NMR signals of the two imido ligands as well as the combustion analysis indicated the reaction product to be a biaryl complex of the proposed structure **9**, **10**.

In order to confirm this proposal, an X-ray single crystal study of **9b** was performed [16], and the structure is shown in Fig. 1. It will be seen that the six-membered lactone has indeed undergone a remarkable ring-expansion with formation of an eight-membered metallacycle, in which the ring-opened biaryl system is coordinated to the metal *via* the two oxygen atoms.

The geometry about the five-coordinate molybdenum center is best described as a distorted tetragonal pyramid with one imido ligand in a basal position and the other occupying the axial site. Interestingly there seems to be greater degree of sp^2 hybridization at the nitrogen of the axial imido ligand than at that in the other one, a feature which is reflected in the much smaller M–N–C bond angle (148.4° compared with 170.0°). Since there is only a small difference in the two Mo–N bond lengths (1.738 Å and 1.723 Å, respectively), which are both characteristic of Mo≡N triple bonds [17], we consider that the bending of the axial Mo–N–C linkage is caused mainly by crystal packing effects. Another interesting feature of the molecular



Scheme 3. Preparation of, and bonding situation in the methylenephosphoranyl substituted imido complexes $M(N^tBu)_2(CH{=}PPh_3)Cl$ for M = Mo (**7**), W (**8**).



Scheme 4.

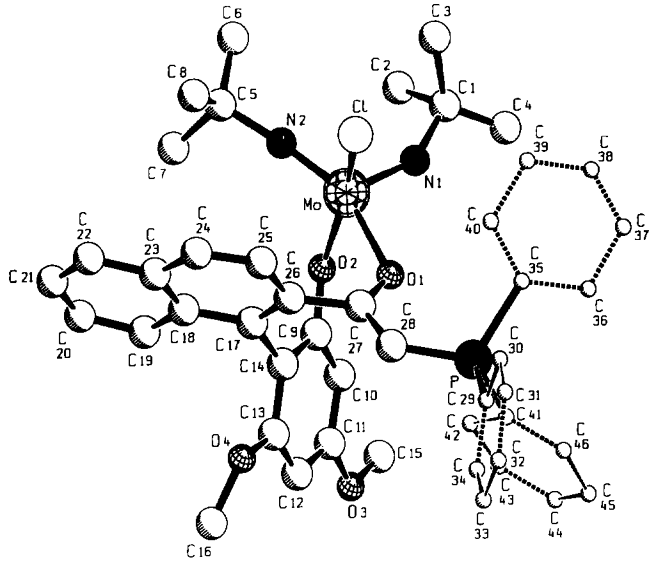


Fig. 1. Structure of **9b** (M = Mo) in the crystal; selected bond lengths (Å) and bond angles (°): Mo–Cl 2.417(3), Mo–O1 2.161(7), Mo–O2 2.003(6), Mo–N1 1.738(9), Mo–N2 1.723(9), N1–C1 1.50(2), N2–C5 1.47(1), P–C28 1.71(1), C27–C28 1.40(1), O1–C27 1.30(1); Cl–Mo–N1 98.4(3), O1–Mo–O2 81.6(3), N1–Mo–N2 109.0(5) Mo–N1–C1 148.4(8), Mo–N2–C5 170.0(7), O1–C27–C26 117.1(9), O1–C27–C28 123.0(1), P–C29–C27 126.9(9).

structure concerns the *O*-bonded acyl-ylide ligand. The relatively short bond distances Mo–O1 (2.161 Å) and C27–C28 (1.40 Å) are a result of substantial enolate character within the Mo–O–C–C array, the bonding situation lying between the two extremes M ← O=CR–CH=PPh_3 and M–O–CR=CH–PPh_3.

The relative position of the two aromatic systems, as defined by the dihedral angle θ (C13–C14–C17–C18), is distinctly enhanced (72.5°) compared with the less twisted starting material **1b** (32.2°) [4], again accounting for the above-mentioned high-field shift in the ^{1}H NMR spectrum.

With respect to the possible use of chiral *C*-nucleophiles for the atropisomer-selective ring-opening of "axially prostereogenic" lactones, a most promising aspect is the fact that the product **9** or **10** is not just a rapidly isomerizering *ortho*-keto-*ortho′*-hydroxy biaryl (*cf.* Scheme 2), but a configuratively more stable eight-membered ring species, which will, as such, certainly not easily collapse to a stereochemically labile six-membered ring.

The helimerization barrier for this metallacycle, the possible atropisomerization-free extrusion of the metal moiety, and the extension of this principle to the use of chiral, optically pure methylenephosphoranyl complexes of molybdenum and tungsten are currently being studied.

Acknowledgements

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14 In a typical example a mixture of 150 mg (0.49 mmol) lactone **1b** and 270 mg (0.49 mmol) complex **6** (M = Mo) in benzene (30 ml) was stirred at 60°C for 3 h and filtered hot. After concentration (10 ml), the product was precipitated by the addition of pentane (30 ml). The yellow powder was filtered off and washed with pentane. Recrystallization from THF/methylcylohexane yielded yellow needles in nearly quantitative yield.

15 Full characterization of all compounds has been provided for referees. Selected data for **9b** (M = Mo) are as follows: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.01$ (s, 9H, C_4H_9), 1.44 (s, 9H, C_4H_9), 3.11 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 4.48 (d, $^{2}J(PH) = 23.5$ Hz, 1H, HC–P). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 29.77$, 31.07 (s, s, $NC(CH)_3$), 54.82, 55.27 (s, s, OCH_3), 64.28 (d, $^{1}J(PC) = 100.3$ Hz, HC–P), 67.73, 70.44 (s, s, NC(CH)$_3$), 189.76 (s, C=C–P). ^{31}P NMR (161 MHz, C_6D_6): $\delta = 13.11$ (s). Anal. Found: C, 64.44; H, 5.25; N, 3.18. $C_{46}H_{48}ClMoN_2O_4P$ (855.26) calc.: C, 64.60; H, 5.66; N, 3.28%.

16 Crystal data for **9b**: $C_{46}H_{48}ClMoN_2O_4P$ (855.26), Enraf–Nonius CAD4, Mo Kα (0.70930 Å), cell constants (293 K): with 23 reflexes ($11° < \theta < 14°$), monoclinic, $P2_1/c$, a 17.103(9) Å, b 12.479(4) Å, c 21.37(1) Å, β 107.84(2)°, $V = 4342$ Å^3, $Z = 4$, $d_{calc.} = 1.30$ g cm^{-3}, $\mu = 4.3$ cm^{-1}, data collection (293 K): ω/θ-Scan, max. $2\theta = 48°$, 7430 ref. measd., 7165 refl. unique, 2478 refl. obs. $[F_o > 2\sigma(F_o)]$; Lp-correction, empirical absorption-correction (ψ-scan method, min. transmission 96.91%); solution by Patterson (SHELXS-86); refinement: full-matrix least-squares, 493 parameter unit weights (Enraf–Nonius SDP), $R = 0.060$, $R_w = 0.057$, rest electron density $+0.497/-0.444$ e Å^{-3}. The complete structural data are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-56451, the names of the authors, and the journal citation.

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