We are presently investigating the binding site of the anion and extending the extraction experiments to different substrates.

*Experimental Section*

The synthesis of **1a** has been described;[1] **1b** was synthesized according to the same procedure. Solutions of enantiopure **1a** or **1b** in $CHCl_3$ ($7 \times 10^{-3}$ mol $L^{-1}$) were shaken at 20 °C with an equivalent volume of solutions of **2**–**6** in water. The layers were separated, and the amount of guest in each layer was determined spectrophotometrically. The HPLC analysis of the enantiomeric excess was carried out on an analytical HSA column.

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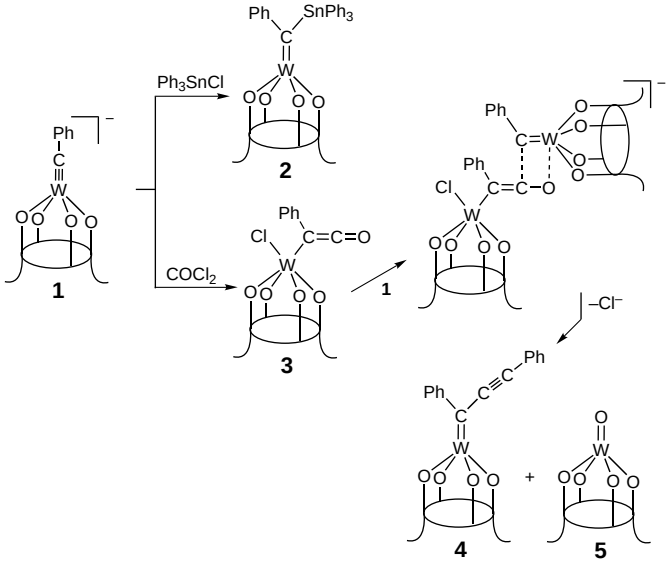
## Functionalizable Alkylidenes: Tungsten Complexes of Phosphanyl-, Amino-, Alkynyl-, and Tinalkylidenes and Their Dimetallic Derivatization**

Silvia Dovesi, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The presence of a heteroatom at the alkylidene carbon atom moves the properties of metal–alkylidene complexes to the borderline of Fischer carbene chemistry.[1] The changes in the M=C bond polarization caused by the heteroatom and the introduction of functional groups increases the possible use of the metal–alkylidene[2] synthon both in organic and organometallic synthesis.[3] Anionic tungsten–alkylidyne derivatives, exemplified by [(cal)W≡CPh] (**1**,[4] $H_4$cal = *p*-*t*Bu-calix[4]arene; Scheme 1), are the appropriate starting materials for




Scheme 1. Synthetic pathways to functionalized alkylidenes. The counterion $M^+$ of the anionic complexes is $Mg_{0.5} \cdot 6$THF.

entering the area of functionalized metal–alkylidenes.[5–7] Two major complementary synthetic routes have been devised to this purpose. The first is the reaction of **1** with a variety of electrophiles, such as $Ph_3SnCl$ (Scheme 1). The tin derivative **2** may be particularly useful in transmetalation reactions with transition metal derivatives. The reaction with $COCl_2$, when carried out with two equivalents of **1**, proceeded straight to an equimolar mixture of **4** and **5**. The difference in

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solubility between **4** and **5** allowed the alkynyl derivative to be easily separated from the oxo compound. When the reaction was carried out with an excess of $COCl_2$, we were able to intercept the intermediate ketenyl derivative **3** (C=C 1.340(7), C=O 1.158(6) Å), which in the presence of one equivalent of **1** led, as expected, to an equimolar mixture of **4** and **5**. Although proceeding by a completely different pathway, the deoxygenation of a ketenyl to an alkynyl functionality has been reported.[8]

The structure of **4** is shown in Figure 1.[9] The calix[4]arene fragment has the expected cone-elliptical conformation for an hexacoordinated metal,[4] and the structural parameters and

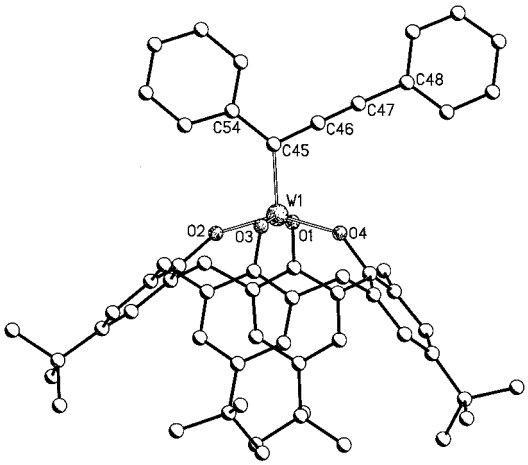
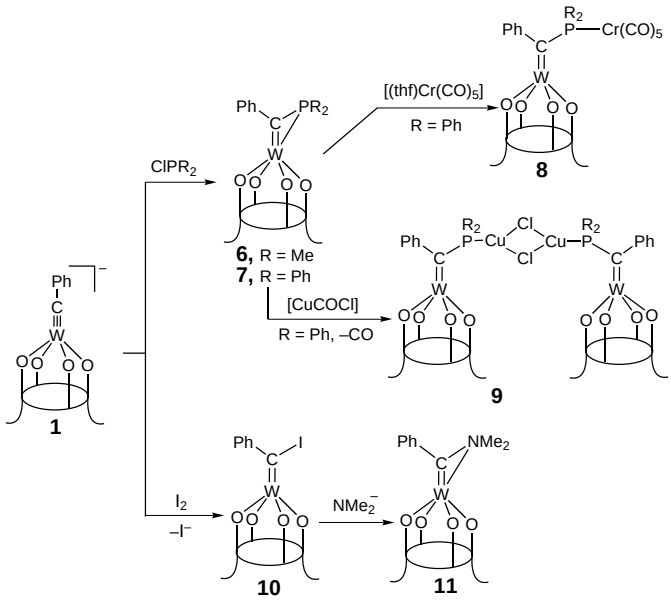



Figure 1. A view of complex **4**; hydrogen atoms have been omitted for clarity, and labels have been used only for the $WO_4$ and the $C_{Ph}$–C–C≡C–$C_{Ph}$ moieties. Selected bond distances [Å]: W1–O1 1.987(5), W1–O2 1.822(5), W1–O3 1.977(5), W1–O4 1.856(5), W1–C45 1.931(7), C45–C46 1.39(1), C46–C47 1.25(1).

spectroscopic data are in agreement with the proposed structure. Complex **4** represents a quite rare case of an alkylidene functionalized with an alkynyl substituent.

The nucleophilicity of **1**, which undergoes reversible protonation/deprotonation and alkylation by $MeOSO_2CF_3$ (MeOTf),[4] has been used for the synthesis of phosphanylalkylidenes[6] and their transformation into dimetallic complexes. The reaction of **1** with $ClPR_2$ (R = Me, Ph) led to **6** and **7** (Scheme 2). The $\eta^2$-phosphanylalkylidenes **6** and **7** maintain the phosphorus atom as an available moiety for intermolecular binding to other metals. This is exemplified by the reaction of **7** with [(thf)$Cr(CO)_5$][10] and [CuCOCl],[11] leading to **8** and **9**, respectively. The complexation by **6** and **7** shows the possibility to assemble dimetallic units around an alkylidene functionality, and indicates how structural parameters change from the uncomplexed to the complexed form. The comparison of the structural parameters of [(cal)W=CHPh][4c,d] with **7**, and then with **8** and **9**, shows interesting trends. The presence of the $PR_2$ group at the alkylidene functionality of **7** results in a lengthening of the W=C bond (from 1.91(2) in [(cal)W=CHPh] to 1.958(4) Å in **7**) and of the W–O bonds. The P–C(alkylidene) bond is particularly short in **7** (1.747(4) Å), and significantly lengthened in **9** (1.839(6) Å), with consequent shortening of the W=C bond (1.906(6) Å). Although the alkylidene moiety has a $\eta^2$-bonding mode in the metallaphosphacyclopropene **7**




Scheme 2. Synthesis of amino- and phosphanylalkylidenes and their dimetallic derivatives. The counterion $M^+$ of the anionic complexes is $Mg_{0.5} \cdot 6\,THF$.

(W–P 2.487(1) Å), a significant contribution comes from the zwitterionic form $[W^{-}–C(Ph)=P^{+}R_2]$.[5] The above parameters and our synthetic method should be compared to the work of Kreissl et al. on cationic tungsten–phosphanylcarbene complexes.[5a,b]

The structure of **9** is shown in Figure 2.[9] The complexation of CuCl led to the cleavage of the metallaphosphacyclopropene ring, restoring the original W=C bond (1.906(6) Å); the W–O bond lengths follow the usual trend, with two long and

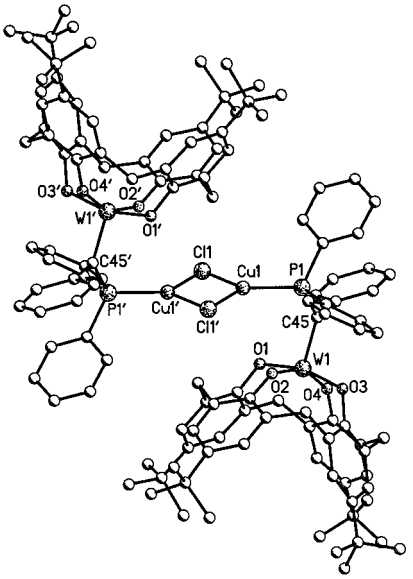



Figure 2. A view of complex **9**; hydrogen atoms and the toluene molecules have been omitted for clarity, and labels have been used only for the metals, the oxygen atoms, and the bridging =C(Ph)–$P(Ph)_2$– moiety. Selected bond distances [Å]: W1–O1 1.964(4), W1–O2 1.852(4), W1–O3 1.970(4), W1–O4 1.856(4), W1–C45 1.906(6), Cu1–Cl1 2.272(2), Cu1–Cl1′ 2.291(2), Cu1–P1 2.166(2), P1–C45 1.839(6). The prime denotes the following symmetry transformation: $-x, -y, -z$.

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two short bonds. The calix[4]arene has the usual regular cone conformation for a pentacoordinated metal.[4]

Another interesting approach to functionalized alkylidenes is reported in Scheme 2, and resembles the methodology leading to functionalized carbynes using starting material of Lalor et al.[12] Oxidation of **1** with $I_2$ led to **10**,[4c] in which the iodine atom can be potentially replaced by a number of organic or organometallic nucleophiles. This approach, using $NaNMe_2$, led to the previously unknown aminoalkylidene **11** (W–C 1.881(7), W–N 2.214(5), C–N 1.416(7) Å).

*Experimental Section*

**4**: The addition of a solution of $COCl_2$ (0.5 mL, 1.93 M, 0.97 mmol) in toluene (100 mL) to a yellow suspension of **1** (2.41 g, 1.77 mmol) in THF (120 mL) gave rise to a dark brown solution. The addition of dioxane (1 mL) provided a suspension, which was stirred overnight at room temperature. The solid, containing magnesium chloride and **5**, was filtered off, and the remaining solution evaporated to dryness to give a brown solid (0.83 g). $^1$H NMR ([D$_6$]benzene, 400 MHz, 298 K): $\delta = 7.93$ (m, 2H; ArH), 7.48 (m, 2H; ArH), 7.34 (m, 2H; ArH), 7.05 (s, 8H; ArH), 7.00 (m, 2H; ArH), 6.67 (m, 1H; ArH), 6.58 (m, 1H; ArH), 5.06 (d, $J = 12.7$ Hz, 4H; *endo*-$CH_2$), 3.21 (d, $J = 12.7$ Hz, 4H; *exo*-$CH_2$), 1.06 (s, 36H; *t*Bu), 0.86 (m, 3H; pentane); $^{13}$C NMR ($CDCl_3$, 298 K): $\delta = 250.9$ (s, $J$(C,W) = 186.4), 153.7 (s, WCC≡CPh). Crystals for X-ray analysis were grown from a solution in pentane.

**7**: A solution of $Ph_2PCl$ (0.94 g, 4.24 mmol) in THF (50 mL) was added dropwise to a yellow suspension of **1** (5.76 g, 4.23 mmol) in THF (160 mL) and dioxane (2 mL), then stirred overnight at room temperature. The remaining solid was filtered off, and the resulting red solution evaporated to dryness. The solid was purified by partial dissolution in toluene (150 mL). The undissolved solid was filtered off, and the remaining solution evaporated to dryness. The final red solid was suspended in pentane and filtered off (50 mL) (70%). Elemental analysis calcd for **7**·0.5 $C_5H_{12}$ ($C_{65.5}H_{73}O_4PW$): C 69.06, H 6.46; found: C 68.9, H 6.44; $^1$H NMR ([D$_6$]benzene, 400 MHz, 298 K): $\delta = 7.97$ (m, 2H; ArH), 7.73 (m, 4H; ArH), 7.28 (m, 2H; ArH), 7.10 (s, 8H; ArH), 6.97 (m, 6H; ArH), 6.78 (m, 1H; ArH), 4.69 (d, $J = 13.2$ Hz, 4H; *endo*-$CH_2$), 3.21 (d, $J = 13.2$ Hz, 4H; *exo*-$CH_2$), 1.09 (s, 36H; *t*Bu), 0.86 (m, 3H, pentane); $^{13}$C NMR ($CD_2Cl_2$, 298 K): $\delta = 249.6$ (d, $J$(C,P) = 37.9); $^{31}$P NMR ([D$_6$]benzene, 298 K): $\delta = -86.8$ (m, $CPPh_2$). Crystals suitable for X-ray diffraction study were grown from a solution in diethyl ether.

**9**: CuCl (0.13 g, 1.31 mmol) was added to a red solution of **7** (1.42 g, 1.24 mmol) in THF (100 mL) at room temperature. When the nitrogen atmosphere was replaced by CO, a dark red solution was obtained. Then the red solution was evaporated to dryness, and the residue suspended in pentane and filtered off (30 mL) (72%). Elemental analysis calcd for **9**·0.5 $C_5H_{12}$ ($C_{128.5}H_{140}Cl_2Cu_2O_8P_2W_2$): C 63.5, H 5.94; found: C 63.3, H 5.78; $^1$H NMR ([D$_6$]benzene, 400 MHz, 298 K): $\delta = 8.48$ (m, 8H; ArH), 8.31 (m, 4H; ArH), 7.31 (m, 6H; ArH), 7.05 (m, 8H; ArH), 6.92 (s, 16H; ArH) overlapping with (m, 2H; ArH), 6.72 (m, 2H; ArH), 4.59 (d, $J = 11.5$ Hz, 8H; *endo*-$CH_2$), 3.04 (d, $J = 11.5$ Hz, 8H; *exo*-$CH_2$), 1.03 (s, 72H; *t*Bu), 0.86 (m, 3H; pentane); $^{13}$C NMR ($CDCl_3$, 298 K): $\delta = 258.1$ (m, CWP); $^{31}$P NMR ([D$_6$]benzene, 298 K): $\delta = 20.4$ (m, $CPPh_2Cu$). Crystals suitable for X-ray diffraction were grown from a solution in toluene.

**11**: Complex **10**[4c] (1.22 g, 1.12 mmol) was added to a solution of $Me_2NLi$ (75.0 mg, 1.14 mmol) in THF (100 mL) at −40 °C to give a brown solution, which was stirred for two days. Volatile components were evaporated from the resulting red solution, and $Et_2O$ (80 mL) added. A white solid was filtered off, volatile components were evaporated, and pentane (40 mL) was added. A solid was then collected and dried in vacuo (68.6%). Elemental analysis calcd for **11** ($C_{55}H_{66}N_2O_4W$; crystals from $Et_2O$/MeCN): C 65.8, H 6.63, N 2.79; found: C 65.9, H 6.67, N 2.62; $^1$H NMR ([D$_6$]benzene, 400 MHz, 298 K): $\delta = 7.53$ (m, 2H; ArH), 7.35 (m, 2H; ArH), 7.18 (s, 8H; ArH), 6.64 (m, 1H; ArH), 4.83 (d, $J = 12.2$ Hz, 4H; *endo*-$CH_2$), 3.40 (s, 6H; $NMe_2$), 3.33 (d, $J = 12.2$ Hz, 4H; *exo*-$CH_2$), 1.20 (s, 36H; *t*Bu), 0.07 (m, 3H; MeCN).

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[9] Crystal structure analysis of **4**: $C_{59}H_{62}O_4W$, $M_r = 1018.94$, monoclinic, space group $P2_1/c$, $a = 13.0869(9)$, $b = 19.9462(8)$, $c = 19.1677(14)$ Å, $\beta = 104.303(6)^\circ$, $V = 4848.3(5)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.396$ g cm$^{-3}$, $F(000) = 2088$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 2.429$ mm$^{-1}$; crystal dimensions $0.34 \times 0.25 \times 0.18$. Diffraction data were collected on a KUMA CCD at 143 K. The structure was solved with direct methods and refined using full-matrix least squares on $F^2$ with all non-hydrogen atoms anisotropically defined. For 6669 observed reflections [$I > 2\sigma(I)$] and 577 parameters, the conventional $R$ is 0.0526 ($wR2 = 0.1276$ for 9094 independent reflections). Crystal structure analysis of **9**: $C_{126}H_{134}Cl_2Cu_2O_8P_2W_2 \cdot 2C_7H_8$, $M_r = 2588.22$, monoclinic, space group $P2_1/c$, $a = 24.459(4)$, $b = 20.052(2)$, $c = 13.013(2)$ Å, $\beta = 102.23(2)^\circ$, $V = 6237.5(15)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.378$ g cm$^{-3}$, $F(000) = 2648$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 2.299$ mm$^{-1}$; crystal dimensions $0.42 \times 0.36 \times 0.31$. Diffraction data were collected on a mar345 Image Plate Detector at 143 K. The structure was solved with direct methods and refined using full-matrix least squares on $F^2$ with all non-hydrogen atoms anisotropically defined. For 9735 observed reflections [$I > 2\sigma(I)$], 689 parameters, and 99 restraints, the conventional $R$ is 0.0505 ($wR2 = 0.1531$ for 11634 independent reflections). Crystallographic data (excluding structure factors) for the structures reported in this paper have been

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deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-119248 (**4**) and CCDC-119249 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Diastereomeric Shape Recognition Using NMR Spectroscopy in a Chiral Liquid Crystalline Solvent

Abdelkrim Meddour, Cécile Canlet, Luis Blanco, and Jacques Courtieu*

The use of NMR spectroscopy in liquid crystalline solvents proved to be a method of choice for enantiomeric analysis.[1] The best results have been obtained with the lyotropic liquid crystals made of organic solutions of a synthetic polypeptide, poly-$\gamma$-benzyl-L-glutamate (PBLG).[2] These lyotropic phases have been known for a long time, and many organic cosolvents such as dichloromethane, chloroform, THF, or DMF can be used.[3]

We have shown that, when dissolved in PBLG liquid crystals, enantiomers are not oriented in the same way.[4] Thus all order-dependant interactions observed by NMR spectroscopy—namely, the chemical shift anisotropies, the dipolar couplings, and the quadrupolar splittings for nuclei with $I > 1/2$, such as deuterium—are affected. With numerous examples, including isotopic chirality, we concluded that this method was more powerful and more general for enantiomeric analysis than any other NMR method.[5]

Induced orientation in liquid crystals is strongly dependent on the shape of the dissolved molecule.[6] Consequently we raised the point whether the molecular order parameters, to which NMR interactions are related, could be used to differentiate molecules that have different shapes. In other words, can NMR spectroscopy be used for shape recognition in liquid crystals?

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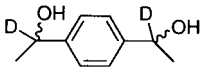
Thinking in terms of shape recognition led us to the problem of distinguishing diastereomers. One could then notice that classical NMR spectroscopy in isotropic solvents does resolve spectra of diastereomers very well, and that no fancy NMR technique in liquid crystals is needed. This remark is true when chiral centers are close to each other. However, when they are separated from each other by four bonds or more this no longer applies, and the problem of distinguishing and attributing *threo-erythro/meso* diastereomers with remote asymmetric groups is exceedingly difficult. Consequently we decided to explore the potential of NMR spectroscopy in PBLG liquid crystals to distinguish diastereomers with remote chiral centers.

We decided to study $\alpha,\alpha'$-dideuterated diol **1**, which exists as the *R*,*R* and *S*,*S* enantiomers and the *R*,*S* *meso* form. The reason is that Takemura et al. reported that the *meso* and *threo* diastereomers of the non-deuterated analogue, where the asymmetric carbon atoms are five bonds apart, cannot be distinguished by $^1$H NMR at 500 MHz or $^{13}$C NMR spectroscopy at 125 MHz.[7] Wallace et al. distinguished such stereoisomers by NMR spectroscopy[8] with their bis($\alpha$-methoxy-$\alpha$-trifluoromethylphenylacetyl) (MTPA) ester derivatives.[9] Still the differences observed were extremely small.[8] Does NMR spectroscopy in PBLG liquid crystals provide an efficient tool to distinguish directly all the stereoisomers for such diols?




**1**

Reduction of 1,4-diacetylbenzene with $NaBD_4$ yielded easily a statistical mixture (25/25/50) of the *R*,*R*/*S*,*S*/*R*,*S* isomers of **1**. Figure 1a shows the $^1$H-decoupled $^2$H NMR spectrum of this mixture in the PBLG/THF liquid crystalline solvent.[10] The spectrum contains four quadrupolar doublets with the same intensities. As each kind of deuterium atom produces a doublet in the $^2$H NMR spectrum measured in PBLG liquid crystals, the interpretation is the following: For the (*R*,*R*)-diol, the two deuterium atoms are homotopic ($C_2$ axis of symmetry), and thus they are magnetically equivalent. Consequently we expect a single doublet, of intensity 2, for this molecule. For the same reason, the *S*,*S* isomer will also furnish a single doublet, of equal intensity but with a different splitting from the signal for the *R*,*R* isomer because of the chiral discrimination. In the achiral *R*,*S* *meso* isomer, things are different. The deuterium nuclei are enantiotopic because they are only related through a symmetry plane. We have recently shown that enantiotopic nuclei are not equivalent in this medium, in contrast to the case of isotropic solvents in classical NMR spectroscopy.[5a, 11] Besides, the probability of obtaining the *R*,*S* form upon reduction of 1,4-diacetylbenzene is twice that of the *R*,*R* or *S*,*S* isomers. Consequently, we expect two doublets, of intensity 2, for this *meso* diol, one doublet for the pro-*R* and one doublet for the pro-*S* deuterium atoms.

To check this interpretation, a mixture of enantiomerically pure (*S*,*S*)-diol[12] with some *R*,*S* diastereomer (*S*,*S*/*R*,*S* = 85/15; Figure 1b) was isolated by chromatography on silica gel of the mixture obtained by transesterification of isopropenyl acetate with the statistical mixture of diol **1** in the presence of the lipase from *pseudomonas cepacia*.[13] To the latter was

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