spectroscopy of ^{15}N-labeled calmodulin. Measurements were made at 15 °C on a Varian Inova 500 MHz NMR spectrometer, and the protein concentration was 1 mM in H_2O/D_2O (9/1) at pH 6.8. Figure 2 displays a small region of $^{15}N-^{1}H$ correlation spectra of calmodulin. Figure 2a shows the conventional HSQC spectrum obtained without the use of

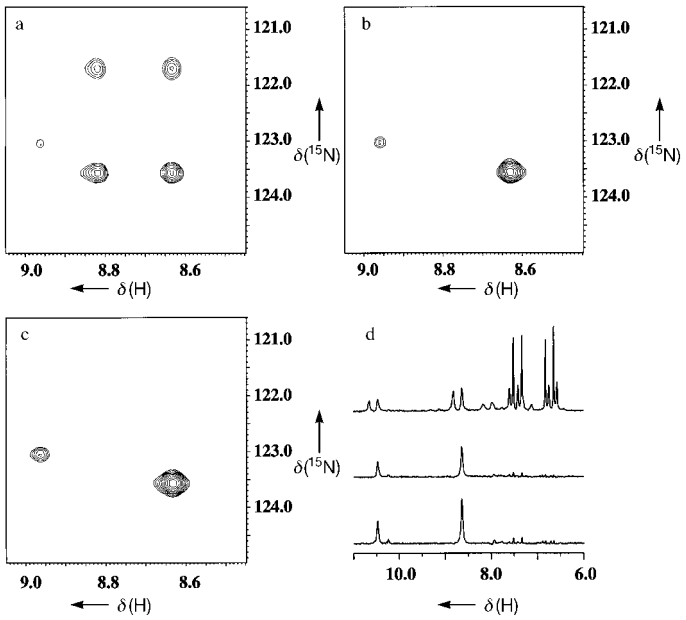

Figure 2. Contour plots of $^{15}N-^{1}H$ correlation spectra of ^{15}N-labeled calmodulin. a) Conventional HSQC spectrum, obtained without decoupling during the t_1 and t_2 periods. b) Spectrum recorded in a conventional TROSY experiment.[4] c) Spectrum recorded in a sensitivity-enhanced TROSY experiment (see text). d) One-dimensional cross sections from the spectra a–c at $\delta(^{15}N) = 123.6$ (from top to bottom). The peaks between 6 and 8 ppm in the HSQC cross section correspond to the cross-peak multiplets at the ^{15}N frequency ($\omega_N - \pi^1 J_{NH}$), which is not observed by TROSY experiments. Spectra b and c, which were recorded and processed with the same parameters, have been scaled to the same noise level. The spacing factor between two consecutive contour lines is 1.2.

decoupling during the t_1 and t_2 periods. It is notable that even at 500 MHz there are significant differences in line width between the four individual multiplets. Figures 2b and 2c are taken from spectra recorded in conventional and sensitivity-enhanced TROSY experiments, respectively. Comparison of Figures 2b and 2c, as well as all other correlation peaks (not shown here), shows that a uniform enhancement in sensitivity of all peaks by a factor of $\sqrt{2}$ was achieved without introducing any artifacts.

The introduction of the TROSY experiment makes NMR spectroscopy a promising technique for studying the structure and function of larger biomolecules. We have improved the sensitivity of the original 2D TROSY experiment by a factor of $\sqrt{2}$ by using different phase cycling and data-processing schemes. This improvement will doubtless have widespread practical application in high-field NMR studies of large proteins.

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[1] a) G. Wagner, *J. Biomol. NMR* **1993**, *3*, 375–385; b) D. Nietlispach, R. T. Clower, R. W. Broadhurst, Y. Ito, J. Keller, M. Kelly, J. Ashurst, H. Oschkinat, P. J. Domaille, E. D. Laue, *J. Am. Chem. Soc.* **1996**, *118*, 407–415.
[2] a) H. M. McConnell, *J. Chem. Phys.* **1956**, *25*, 709–715; b) R. R. Vold, R. L. Vold, *Prog. NMR Spectrosc.* **1978**, *12*, 79–133; c) M. Goldman, *J. Magn. Reson.* **1984**, *60*, 437–452; d) S. Wimperis, G. Bodenhausen, *Mol. Phys.* **1989**, *66*, 897–919; e) J. Boyd, U. Hommel, I. D. Campbell, *Chem. Phys. Lett.* **1990**, *175*, 477–482.
[3] a) L. E. Kay, L. K. Nicholson, F. Delaglio, A. Bax, D. A. Torchia, *J. Magn. Reson.* **1992**, *97*, 359–375; b) A. G. Palmer, N. J. Skelton, W. J. Chazin, P. E. Wright, M. Rance, *Mol. Phys.* **1992**, *75*, 699–711; c) N. Tjandra, A. Szabo, A. Bax, *J. Am. Chem. Soc.* **1996**, *118*, 6986–6991.
[4] K. Pervushin, R. Riek, G. Wider, K. Wuthrich, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 12366–12371.
[5] a) A. G. Palmer III, J. Cavanagh, P. E.Wright, M. Rance, *J. Magn. Reson.* **1991**, *93*, 151–170; b) J. Cavanagh, M. Rance, *J. Magn. Reson.* **1990**, *88*, 72–85; c) L. E. Kay, P. Keifer, T. Saarinen, *J. Am. Chem. Soc.* **1992**, *114*, 10663–10665; d) J. Schleucher, M. Sattler, C. Griesinger, *Angew. Chem.* **1993**, *105*, 1518–1521; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1489–1491.
[6] a) R. R. Ernst, G. Bodenhausen, A. Wokaun, *The Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon, Oxford, **1987**; b) O. W. Sorensen, G. W. Eich, M. H. Levitt, G. Bodenhausen, R. R. Ernst, *Prog. NMR Spectrosc.* **1983**, *16*, 163–192.
[7] D. I. States, R. A. Haberkorn, D. J. Buben, *J. Magn. Reson.* **1982**, *93*, 151.
[8] Note added in proof: A reviewer's comments alerted us to a difference between Varian and Bruker spectrometers, which requires that the *y*-axis receiver phases be inverted. It is also necessary to invert the *y*-axis pulse phases. In the pulse sequence of Figure 1, the particular phase cycling means that only the phase of the second 90° ^{1}H pulse needs to be considered. For optimal sensitivity, the phase of this pulse should be $-y$ for Varian and $+y$ for Bruker. If this phase is inverted then the "steady-state" enhancement, described by Pervushin et al. (*J. Am. Chem. Soc.* **1998**, *120*, 6394–6400) after this manuscript was submitted, will be lost. The sensitivity enhancement presented in this work is independent of the phase of this pulse and a $\sqrt{2}$ enhancement is gained over the corresponding TROSY experiment that has the same phase for this pulse.

Directed Positioning of Organometallic Fragments Inside a Calix[4]arene Cavity

Catherine Wieser-Jeunesse, Dominique Matt,* and André De Cian

A major attraction of cone-shaped calix[4]arenes concerns the presence of a macrocyclic cavity defined by four symmetrically sited phenoxy rings.[1] To date, exploitation of such organized structures has mostly relied on converging π systems on the inner side that facilitate weak binding of various substrates,[2] including certain metal cations.[3] Surprisingly, despite increasing interest in the application of calixarenes as ligands in transition metal chemistry,[4] the

[*] Dr. D. Matt, Dr. C. Wieser-Jeunesse
Université Louis Pasteur, UMR 7513 CNRS
Groupe de Chimie Inorganique Moléculaire
1 rue Blaise Pascal, F-67008 Strasbourg Cedex (France)
Fax: (+33) 3-88-617852
E-mail: dmatt@chimie.u-strasbg.fr
Dr. A. De Cian
Université Louis Pasteur, UMR 7513 CNRS
Laboratoire de Cristallochimie et Chimie Structurale
4 rue Blaise Pascal, F-67008 Strasbourg Cedex (France)

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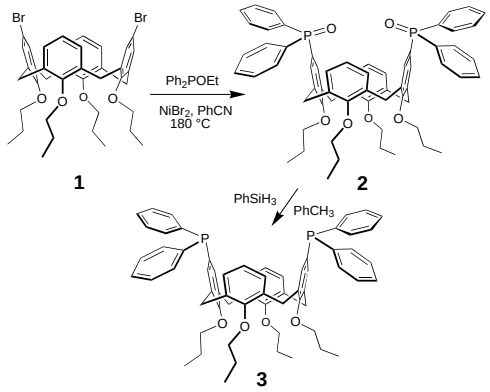
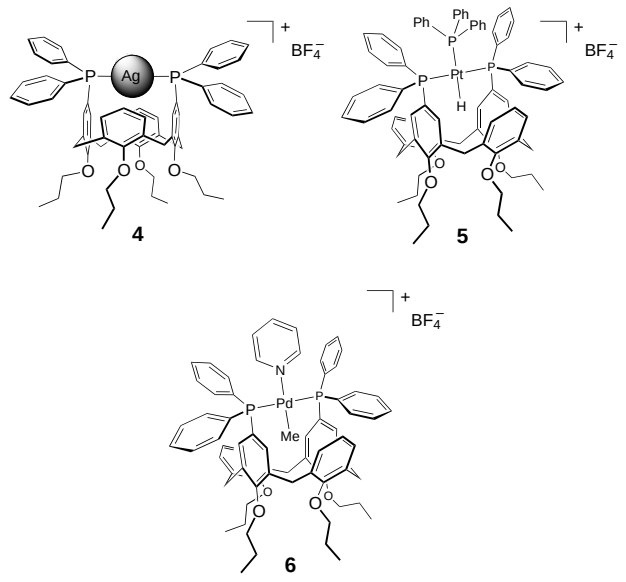
interior of the cavity has not been used to entrap or confine reactive fragments bound to transition metal ions.[5] Such architectures could possess the capability to promote metal-centered reactions that are sterically constrained, thereby allowing combined shape control and regioselectivity.[6] Furthermore, it is likely that the cavity walls will afford protection of highly reactive "M–R" units against undesired side reactions. We now report the first calix[4]arenes with organometallic fragments positioned inside the larger opening of the cavity.

Our approach to the construction of such systems exploits the coordinative properties of the hemispherical ligand **3**, a calix[4]arene bearing two P^{III} centers located on distal *p*-carbon atoms of the upper rim. Diphosphane **3** was conveniently prepared in two steps from **1**[7] by using well-established procedures:[8] diphosphorylation of **1** with $Ph_2POEt/NiBr_2$ resulted in formation of the di(phosphane oxide) **2**, which was then quantitatively reduced with $PhSiH_3$ to afford **3** (Scheme 1).



Scheme 1. Synthesis of the hemispherical ligand **3** in two steps.

Diphosphane **3** seems to be an ideal scaffold on which to assemble *trans*-chelate complexes: for example it reacts with one equivalent of $AgBF_4$ to form complex **4**. The FAB mass spectrum of **4** exhibits an intense signal at *m*/*z* 1069.6 with the appropriate isotopic profile for the $(\mathbf{4}-BF_4)^+$ ion. NMR data collected for **4** show the molecule to possesses C_2 symmetry,



with the chemical shift found for the ^{31}P NMR signal being exactly as expected for the assigned structure.[9]

The above studies serve to indicate, not unsurprisingly, that the phosphane groups remain readily accessible for complexation with Ag^+ ions; more challenging targets were then sought. Treatment of **3** with $[PtH(thf)(PPh_3)_2]^+$ in refluxing THF afforded the platinum(II) complex **5** quantitatively. As for **4**, the ^1H and ^{13}C NMR data indicate an apparent C_2-symmetry for the calixarene skeleton. Furthermore, the ^{31}P NMR spectrum unambigously establishes the *trans*-spanning behavior of the diphosphane as well as the presence of two types of phosphorus atoms (the phosphorus atoms on the calixarene appear as a doublet with ^{195}Pt satellites at $\delta = 15.0$; $J(P,P') = 20$ Hz, $J(P,Pt) = 2706$ Hz). The bulky PPh_3 ligand, positioned *trans* to the hydride ligand, forces the Pt–H bond to point inside the calixarene cavity. The signal for the hydride atoms appears approximately 1.3 ppm upfield with respect to the related $[PtH(PPh_3)_3]^+$ ion,[10] thus reflecting the high shielding effect of the two phenoxy rings that border the hydride atom. In contrast to other complexes of the type $[PtH(PPh_3)(\widehat{P\,P})]^+$ that contain a *trans*-spanning diphosphane,[11] complex **5** is inert towards *cis*/*trans* isomerization in solution. Since only the *trans* isomer has the necessary stereochemical features to position the hydride atom group inside the cavity, the reluctance to isomerize attests to the stability of the inclusion complex.

With the aim to entrap larger metallo-fragments inside the cavity, a solution of **3** in THF was treated with the cationic alkylpalladium complex $[PdMe(cod)(thf)]BF_4$ (cod = cyclooctadiene). Subsequent addition of pyridine resulted in the quantitative formation of complex **6**. Characteristic features of the ^1H NMR spectrum are the presence of a triplet for the methyl group at $\delta = -0.79$, a solitary AB quartet for the $ArCH_2Ar$ bridges, and a virtual triplet for four (*o*-*P*)–Ar*H* hydrogen atoms ($|{}^3J(PH)+{}^5J(PH)| = 9$ Hz). In the ^{31}P NMR spectrum the phosphorus atoms appear as a singlet at $\delta = 27.0$. Two-dimensional NOESY spectra (500 MHz) indicate that the methyl hydrogen atoms lie in close proximity to the phenolic CH bonds of the two phosphorus-substituted phenoxy rings. Taking into account that the bulky pyridine ligand does not allow gyroscopic spinning of the pyridine-Pd-Me fragment around the P–P axis, these findings clearly establish that the methyl group is locked inside the cavity.

A further illustration of the unique complexing properties of calixarene **3** concerns the positioning of octahedral metal centers at the entrance of the cavity. Treatment of commercial ruthenium trichloride with carbon monoxide in boiling ethoxyethanol followed by the addition of **3** afforded the Ru^{II} complex **7** in high yield (Scheme 2). The *cis* arrangement of the two carbonyl units was inferred from the infrared spectrum, which showed two absorption bands in the CO region ($\tilde{\nu} = 2072$(s) and 1995(s) cm^{-1}). Complex **7** slowly isomerizes in 1,2-dichloroethane into the *trans,trans,trans* isomer **8** ($\tilde{\nu}(C{\equiv}O) = 1924$(s) cm^{-1}). The *trans*-spanning behavior of the diphosphane was confirmed by an X-ray diffraction study (Figure 1). The most remarkable feature of this structure is the entrapment of one metal carbonyl unit inside the calixarene cavity, the CO ligand being exactly intercalated

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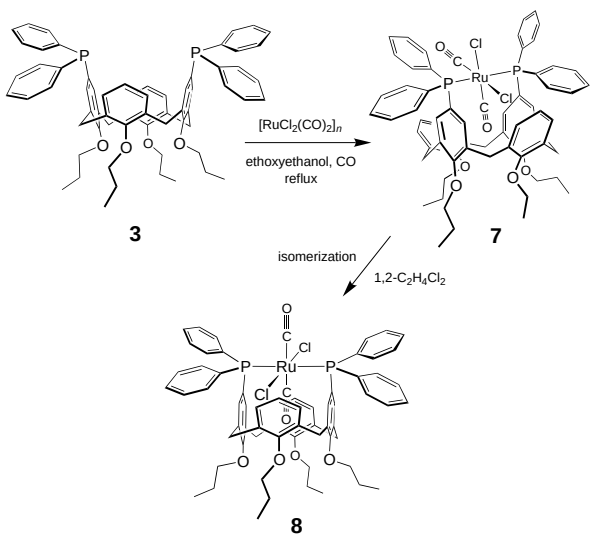

Scheme 2. Positioning of octahedral ruthenium units at the mouth of calixarene **3**.

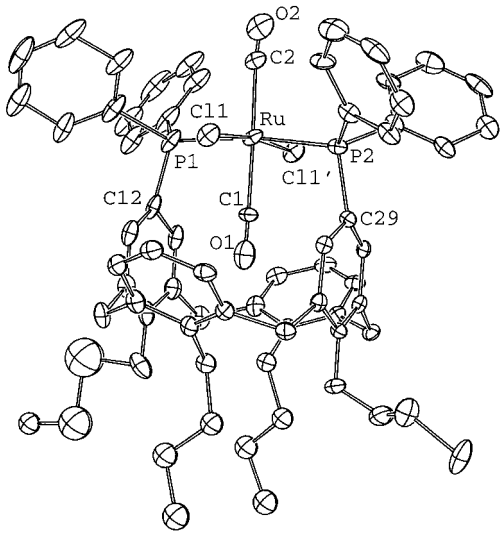

Figure 1. Structure of complex **8** (ORTEP). Selected bond lengths [pm] and angles [°]: Ru – P1 240.9(5), Ru – P2 240.3(5), Ru – C1 196(2), Ru – C2 188(2), Ru – Cl 241.0(3), P1 – C12 182(2), P2 – C29 184(1); P1-Ru-P2 172.2(3), Cl-Ru-Cl 171.9(2), Ru-P(1)-C(12) 106.6(5), Ru-P(2)-C(29) 107.2(5). The molecule possesses a mirror plane containing the phosphorus and ruthenium atoms. Each carbon atom of the propyl groups that are linked to the OArP rings are disordered over two positions.

between the two bordering P-substituted phenyl rings. The distance between these planes and the CO ligand axis is rather short (about 2.75 Å), thus suggesting a bonding interaction between the sandwiched CO and the two PPh rings. The relatively low $\tilde{\nu}$(CO) frequency (1924(s) cm^{-1} compared with 1998 cm^{-1} for *trans,trans,trans*-$[RuCl_2(CO)_2(PPh_3)_2]$[12]) supports this assumption.

Experimental Section

All reactions were carried out in dry solvents under purified nitrogen.

2: Yield: 82 %; m.p. > 280 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.76 – 7.69 and 7.54 – 7.48 (20 H, PPh_2), 7.40 (d, 4 H, *m*-H of OArP, ^3J(P,H) = 12 Hz), 6.24 and 6.02 (AB_2 spin system, 6 H, *m*- and *p*-H of OAr, ^3J = 7.5 Hz), 4.42 and 3.12 (AB spin sytem, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 4.08 (pseudo t, 4 H, OCH_2, $^3J \approx 8$ Hz), 3.60 (t, 4 H, OCH_2, ^3J = 8 Hz), 1.94 (m, 4 H, OCH_2CH_2), 1.82 (m, 4 H, OCH_2CH_2), 1.06 (t, CH_3, ^3J = 8 Hz), 0.90 (t, CH_3, ^3J = 8 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 161.52 and 155.12 (2s, arom. C_q – O), 137.67 – 122.31 (arom. C atoms), 77.14 and 76.74 (2s, OCH_2), 30.96 (s, ArCH_2), 23.51 and 23.17 (2s, CH_2CH_3), 10.84 and 9.86 (2s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 29.4 (s, PPh_2); elemental analyses calcd for $C_{64}H_{66}O_6P_2 \cdot 0.5\,CHCl_3$ (993.18 + 59.69): C 73.58, H 6.37; found: C 74.00, H 6.37.

3: Yield: 75 %; m.p. 230 – 233 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.37 – 7.33 (20 H, PPh_2), 7.06 (d, 4 H, *m*-H of OArP, ^3J(P,H) = 8 Hz), 6.29 and 6.11 (AB_2 spin system, 6 H, *m* and *p*-H of OAr, ^3J = 8 Hz), 4.41 and 3.06 (AB spin sytem, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 4.03 (pseudo t, 4 H, OCH_2, $^3J \approx 8$ Hz), 3.63 (t, 4 H, OCH_2, ^3J = 8 Hz), 2.00 (m, 4 H, OCH_2CH_2), 1.81 (m, 4 H, OCH_2CH_2), 1.06 (t, CH_3, ^3J = 7.5 Hz), 0.91 (t, CH_3, ^3J = 7.5 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 159.80 and 155.10 (2s, arom. C_q – O), 137.25-122.02 (arom. C atoms), 77.00 and 76.60 (2s, OCH_2), 30.94 (s, ArCH_2Ar), 23.51 and 23.15 (2s, CH_2CH_3), 10.82 and 9.93 (2s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = – 6.4 (s, PPh_2); elemental analyses calcd for $C_{64}H_{66}O_4P_2$ (961.18): C 79.98, H 6.92; found: C 80.18, H 6.74.

4: Yield: 80 %; m.p. 187 – 190 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43-7.37 (24 H, arom. H), 6.82 (s, 4 H, *m*-H of OArP), 6.18 (t of B_2A spin system, 2 H, *p*-H of OAr, ^3J = 8 Hz), 4.40 and 3.05 (AB spin system, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 4.01 (pseudo t, 4 H, OCH_2, $^3J \approx$ 8 Hz), 3.70 (t, 4 H, OCH_2, ^3J = 8 Hz), 1.98 (m, 4 H, OCH_2CH_2), 1.89 (m, 4 H, OCH_2CH_2), 1.09 (t, CH_3, ^3J = 7.5 Hz), 0.83 (t, CH_3, ^3J = 7.5 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 157.18 and 156.85 (2s, arom. C_q – O), 136.09-123.02 (arom. C atoms), 77.64 and 76.59 (2s, OCH_2), 30.85 (s, ArCH_2Ar), 23.91 and 23.57 (2s, CH_2CH_3), 10.79 and 9.80 (2s, CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 10.4 (two d, PPh_2, $J(^{107}Ag,P)$ = 503 Hz, $J(^{109}Ag,P)$ = 580 Hz); MS (FAB): *m/z* calcd for $C_{64}H_{66}O_4P_2Ag$ [*M* – BF_4]: 1069; found 1069.6; elemental analyses calcd for $C_{64}H_{66}BF_4O_4P_2Ag$ (1155.86): C 66.51, H 5.76; found: C 66.66, H 5.43.

5: Yield: 73 %; m.p. 226 – 230 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.42 – 7.02 and 6.87 (43 H, arom. H), 6.24 (t of B_2A spin system, 2 H, *p*-H of OAr, ^3J(A,B) = 6 Hz), 4.44 and 3.09 (AB spin sytem, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 4.04 (pseudo t, 4 H, OCH_2, $^3J \approx 6$ Hz), 3.69 (t, 4 H, OCH_2, ^3J = 7 Hz), 1.97 (m, 4 H, OCH_2CH_2), 1.89 (m, 4 H, OCH_2CH_2), 1.10 (t, CH_3, ^3J = 9 Hz), 0.92 (t, CH_3, ^3J = 7 Hz), – 6.93 (dt with Pt satellites, 1 H, PtH, $^2J(H,P_{cis})$ = 17 Hz, $^2J(H,P_{trans})$ = 167 Hz); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ = 157.39 and 156.70 (2s, arom.C_q – O), 136.40 – 122.43 (arom. C atoms), 77.90 and 76.65 (2s, OCH_2), 30.93 (s, ArCH_2), 23.51 and 22.94 (2s, CH_2CH_3), 10.74 and 9.77 (2s, CH_2CH_3); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 °C): δ = 24.2 (t with Pt satellites, PPh_3, ^2J(P,P′) = 20 Hz, J(P,Pt) = 2120 Hz), 15.0 (d, PPh_2, ^2J(P,P′) = 20, J(P,Pt) = 2706 Hz). MS (FAB): *m/z* calcd for $C_{82}H_{82}O_4P_3Pt$ [*M* – BF_4]: 1418.5; found: 1418.8 (expected isotopic profile); elemental analyses calcd for $C_{82}H_{82}BF_4O_4P_3Pt$ (1506.38): C 65.38, H 5.49; found: C 65.18, H 5.43.

6 : Yield: 81 %; m.p. 163 – 166 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 7.79 (d, 2 H, *o*-H of pyridine), 7.52 (t, 1 H, *p*-H of pyridine, ^3J = 5 Hz), 7.32 – 7.24 (20 H, PPh_2), 7.06 – 7.00 (m, 6 H, *m*- and *p*-H of OAr), 6.79 (m br, 2 H, *m*-H of pyridine), 6.62 (virtual t, 4 H, AA′XX′A″A‴ spin system (X = P), 4 H, *m*-H of OArP, $|^3J$(P,H)+^5J(P′,H)$|$ = 9 Hz), 4.56 and 3.24 (AB spin sytem, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 4.15 (pseudo t, 4 H, OCH_2, $^3J \approx 8$ Hz), 3.81 (t, 4 H, OCH_2, ^3J = 7 Hz), 2.06 (m, 4 H, OCH_2CH_2), 1.97 (m, 4 H, OCH_2CH_2), 1.15 (t, CH_3, ^3J = 7 Hz), 0.96 (t, CH_3, ^3J = 7 Hz), – 0.79 (t, 3 H, Pd-CH_3, J(P,H) = 6 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 50 MHz, 25 °C): δ = 157.95 and 157.59 (2s, arom. C_q – O), 151.66 – 121.56 (arom. C atoms), 78.32 and 77.08 (2s, OCH_2), 31.32 (s, ArCH_2Ar), 23.98 (s, CH_2CH_3), 11.00 and 9.98 (2s, CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 25 °C): δ = 27.0 (s, PPh_2) MS (FAB): *m/z* calcd for $C_{65}H_{69}O_4P_2Pd$ [*M* – pyridine – BF_4]: 1081; found: 1081.1 (expected isotopic profile); elemental analyses calcd for $C_{70}H_{74}BF_4NO_4P_2Pd$ (1248.53): C 67.34, H 5.95, N 1.12; found: C 67.41, H 6.10, N 0.93.

7 : Yield: 84 %; m.p. > 280 °C; IR (KBr): $\tilde{\nu}$(C≡O) = 2072(s) and 1995(s) cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.31 – 8.28 and 7.36 – 7.34 (20 H, PPh_2), 6.82 (virtual t, 4 H, *m*-H of OArP), 6.81 and 6.65 (B_2A spin system, 6 H, *m*- and *p*-H of OAr, ^3J(A,B) = 6 Hz), 4.47 and 3.19 (AB spin sytem, 8 H, ArCH_2Ar, ^2J(A,B) = 13 Hz), 3.99 (pseudo t, 4 H,

OCH_2, $^3J \approx 8$ Hz), 3.78 (t, 4H, OCH_2, $^3J = 7$ Hz), 2.02 (m, 4H, OCH_2CH_2), 1.94 (m, 4H, OCH_2CH_2), 1.11 (t, CH_3, $^3J = 7.5$ Hz), 0.91 (t, CH_3, $^3J = 9$ Hz); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): $\delta = 158.48$ and 157.75 (2s, arom.C_q–O), 135.02–123.95 (arom. C atoms), 78.47 and 76.79 (2s, OCH_2), 31.09 (s, ArCH_2), 23.95 and 23.51 (2s, CH_2CH_3), 11.05 and 10.01 (2s, CH_2CH_3), C≡O not detected; $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): $\delta = 12.9$ (s, PPh_2); MS (FAB): *m/z* calcd for $C_{65}H_{66}ClO_5P_2Ru$ [M – Cl – (CO)]: 1125; found: 1125.5 (expected isotopic profile); elemental analyses calcd for $C_{66}H_{66}Cl_2O_6P_2Ru$ (1189.18): C 66.66, H 5.59; found: C 66.54, H 5.63.

8: Yield: 95%; IR (KBr): $\tilde{\nu}$(C≡O) = 1924(s) cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 7.91$–7.89 and 7.37–7.35 (20H, PPh_2), 6.86 and 6.67 (B_2A spin system, 6H, *m*- and *p*-H of OAr, $^3J(A,B) = 7.5$ Hz), 6.75 (virtual t ABXX′A′B′ spin system, 4H, *m*-H of OArP, $^3J(A,X) \approx {}^3J(B,X) \approx 5$ Hz), 4.51 and 3.22 (AB spin sytem, 8H, ArCH_2Ar, $^2J(A,B) = 13$ Hz), 4.14 (pseudo t, 4H, OCH_2, $^3J \approx 8$ Hz), 3.79 (t, 4H, OCH_2, $^3J = 7$ Hz), 2.01 (m, 4H, OCH_2CH_2), 1.95 (m, 4H, OCH_2CH_2), 1.13 (t, CH_3, $^3J = 7.5$ Hz), 0.90 (t, CH_3, $^3J = 9$ Hz); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): $\delta = 42.4$ (s, PPh_2). Crystal data for $\mathbf{8} \cdot C_2H_4Cl_2$: $M_r = 1288.14$, orthorombic, space group *Pbcm*, $a = 19.4779(6)$, $b = 17.7412(3)$, $c = 17.2124(5)$ Å, $V = 5947.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.44$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.544$ mm^{-1}. Data were collected on a Kappa CCD Enraf Nonius system at 173 K. The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. $R1 = 0.089$ and $wR2 = 0.117$ for 3296 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101566. 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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[1] For example, see "Calixarenes": C. D. Gutsche in *Monographs in Supramolecular Chemistry, Vol. 1* (Ed.: J. F. Stoddart), Royal Society of Chemistry, Cambridge, **1989**; V. Böhmer, *Angew. Chem.* **1995**, *107*, 785–818; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713–745; M. A. van Wageningen, E. Snip, W. Verboom, D. N. Reinhoudt, H. Boerrigter, *Liebigs Ann.* **1997**, 2235–2245.

[2] For example, see R. Ungaro, A. Pochini, G. Andreeti, P. Domiano, *J. Chem. Soc. Perkin Trans. 2* **1985**, 197–201; W. Xu, R. J. Puddephatt, L. Manojlovic-Muir, K. W. Muir, C. S. Frampton, *J. Incl. Phenom.* **1994**, *19*, 277–290; V. C. Gibson, C. Redshaw, W. Clegg, M. R. J. Elsegood, *J. Chem. Soc. Chem. Commun.* **1995**, 2371–2372; J. L. Atwood, K. T. Holman, J. W. Steed, *Chem. Commun.* **1996**, 1401–1407; P. D. Beer, M. G. B. Drew, P. B. Leeson, M. I. Ogden, *Inorg. Chim. Acta* **1996**, *246*, 133–141; C. L. Raston, J. L. Atwood, P. J. Nichols, I. B. N. Sudria, *Chem. Commun.* **1996**, 2615–2616; R. Abidi, M. V. Baker, J. M. Harrowfield, D. S.-C. Ho, W. R. Richmond, B. W. Skelton, A. H. White, A. Varnek, G. Wipff, *Inorg. Chim. Acta* **1996**, *246*, 275–286; A. Ikeda, Y. Suzuki, M. Yoshimura, S. Shinkai, *Tetrahedron* **1998**, *54*, 2497–2508.

[3] A. Ikeda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 3102–3110.

[4] D. V. Khasnis, J. M. Burton, J. D. McNeil, H. Zhang, M. Lattman, *Phosphorus Sulfur Silicon* **1993**, *75*, 253–256; C. Dieleman, C. Loeber, D. Matt, A. De Cian, J. Fischer, *J. Chem. Soc. Dalton Trans.* **1995**, 3097–3100; D. M. Roundhill, *Progr. Inorg. Chem.* **1995**, *43*, 533–592; I. Neda, H.-J. Plinta, R. Sonnenburg, A. Fischer, P. G. Jones, R. Schmutzler, *Chem. Ber.* **1995**, *128*, 267–273; B. R. Cameron, S. J. Loeb, *Chem. Commun.* **1996**, 2003–2004; C. Loeber, D. Matt, P. Briard, D. Grandjean, *J. Chem. Soc. Dalton Trans.* **1996**, 513–524; C. Wieser, D. Matt, J. Fischer, A. Harriman, *J. Chem. Soc. Dalton Trans.* **1997**, 2391–2402; M. Giusti, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Organometallics* **1997**, *16*, 5610–5612; A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Chem. Commun.* **1997**, 183–184; C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93–161.

[5] A homooxacalix[4]arene-Eu complex containing a coordinated acetone molecule that is located inside the cavity has been reported: Z. Asfari, J. M. Harrowfield, M. I. Ogden, J. Vicens, A. H. White, *Angew. Chem.* **1991**, *103*, 887–889; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 854–856.

[6] H. K. A. C. Coolen, P. W. N. M. van Leeuwen, R. J. M. Nolte, *Angew. Chem.* **1992**, *104*, 906–909; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 905–907; M. T. Reetz, S. R. Waldvogel, *Angew. Chem.* **1997**, *109*, 870–873; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 865–867; K. Goto, R. Okazaki, *Liebigs Ann.* **1997**, 2393–2407.

[7] M. Larsen, M. Jørgensen, *J. Org. Chem.* **1996**, *61*, 6651–6655.

[8] V. I. Kalchenko, L. I. Atamas, V. V. Pirozhenko, L. N. Markovsky, *Zh. Obshch. Khim.* **1992**, *62*, 2623–2625; S. Ozegowski, B. Costisella, J. Gloede, *Phosphorus Sulfur Silicon.* **1996**, *119*, 209–223; C. Loeber, C. Wieser, D. Matt, A. De Cian, J. Fischer, L. Toupet, *Bull. Soc. Chim. Fr.* **1995**, *132*, 166–177.

[9] M. Camalli, F. Caruso, S. Chaloupka, P. N. Kapoor, P. S. Pregosin, L. M. Venanzi, *Helv. Chim. Acta* **1984**, *67*, 1603–1611.

[10] K. Thomas, J. T. Dumler, B. W. Renoe, C. J. Nyman, D. M. Roundhill, *Inorg. Chem.* **1972**, *11*, 1795–1799.

[11] G. Bracher, D. M. Grove, L. M. Venanzi, F. Bachechi, P. Mura, L. Zambonelli, *Helv. Chim. Acta* **1980**, *63*, 2519–2530.

[12] R. Vac, J. H. Nelson, E. B. Milosavljević, L. Solujić, *Inorg. Chem.* **1989**, *28*, 3831–3836.

A New Radical Allylation Reaction of Dithiocarbonates**

Béatrice Sire, Stéphanie Seguin, and Samir Z. Zard*

In contrast to radical cyclizations, which have practically revolutionized the construction of polycyclic systems, intermolecular radical additions to olefins have had a comparatively limited impact on organic synthesis.[1] This is chiefly because of the difficulty in avoiding competing bimolecular side reactions which, in the case of intramolecular processes, can usually be controlled by the use of high dilution techniques (e.g. slow, syringe pump addition of one of the reagents). With stannane-based reactions, for example, the difficulty lies in preventing premature hydrogen atom transfer to the radical before it adds to the olefin. One special exception is the allylation reaction with allyltriorganotin.[2] In this case, the allyl transfer step is the one that regenerates the stannyl radical to propagate the chain and, even if this step is not very fast by radical reaction standards,[3] there are no other major competing pathways. This fairly general and quite useful intermolecular C–C bond forming procedure unfortunately uses tin and therefore suffers from the same drawbacks as other tin-based systems: high cost and difficulty in removing toxic organotin contaminants.[4] These are serious

[*] Dr. S. Z. Zard,[+] Dr B. Quiclet-Sire, S. Seguin
Institut de Chimie des Substances Naturelles
91198 Gif-Sur-Yvette (France)
Fax: (+33) 1-69-07-72-47

[+] Further address:
Laboratoire de Synthèse Organique associé au CNRS
Ecole Polytechnique, 91128 Palaiseau Cedex (France)
Fax: (+33) 1-69-33-30-10

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