B. J. Dunne, R. B. Morris, A. G. Orpen, *J. Chem. Soc. Dalton Trans.* **1991**, 653, and references therein.

[2] a) X. Li, S. I. Weissman, T.-S. Lin, P. P. Gaspar, *J. Am. Chem. Soc.* **1994**, *116*, 7899, and references therein; b) E. Niecke, J. Böske, D. Gudat, W. Güth, M. Lysek, E. Symalla, *Nova Acta Leopold.* **1985**, *59*, 83.

[3] a) X. Li, K. D. Robinson, P. P. Gaspar, *J. Org. Chem.* **1996**, *61*, 7702; b) N. Mezailles, P. E. Fanwick, C. P. Kubiak, *Organometallics* **1997**, *16*, 1526.

[4] A. Marinetti, F. Mathey, L. Ricard, *Organometallics* **1993**, *12*, 1207.

[5] a) See stable isomers of phosphabenzenes and oligomers of *t*BuC≡P containing PC_2 rings: M. Regitz in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. Scherer), Thieme, Stuttgart, **1990**, p. 79; b) D. Hu, H. Schäufele, H. Pritzkow, U. Zenneck, *Angew. Chem.* **1989**, *101*, 929; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 900. Also, P_4 is a quite stable molecule.

[6] a) (Hoffmann-La Roche), NL-B 6600093, **1966**, [*Chem. Abstr.* **1967**, *66*, 2426]; b) H. Kessler, *Methoden der Organischen Chemie* (*Houben-Weyl*), 4th ed. 1952–, *Vol. 5/1d*, **1972**, pp. 301.

[7] P-Amino phosphiranes see: a) E. Niecke, W. W. Schoeller, D.-A. Wildbredt, *Angew. Chem.* **1981**, *93*, 119; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 131; b) E. Niecke, M. Leuer, M. Nieger, *Chem. Ber.* **1989**, *122*, 453.

[8] J. Thomaier, S. Boulmaâz, H. Schönberg, H. Rüegger, A. Currao, H. Grützmacher, H. Hillebrecht, H. Pritzkow, *New J. Chem.* **1998**, *21*, 947.

[9] D. C. R. Hockless, M. A. McDonald, M. Pabel, S. B. Wild, *J. Chem. Soc. Chem. Commun.* **1995**, 257.

[10] a) D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey, L. Ricard, *J. Chem. Soc. Dalton Trans.* **1993**, 1811, and references therein; b) S. S. Al Juaid, D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey, J. F. Nixon, *J. Chem. Soc. Dalton Trans.* **1991**, 905.

[11] a) All structures were solved by direct methods and refined against full-matrix (versus F^2) with SHELXTL (Version 5.0). **5b**: orthorhombic, space group $P2_12_12_1$; $a = 8.829(1)$, $b = 8.887(1)$, $c = 25.544(4)$ Å; $V = 2004.3(5)$ Å^3; $Z = 4$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 56.6°$. 16654 reflections, 4975 independent ($R_{int.} = 0.0543$); $R_1 = 0.0531$, $wR_2 = 0.1136$ (based on F^2) for 309 parameters and 3598 reflections with $I > 2\sigma(I)$. **6**: monoclinic, space group $P2_1/n$; $a = 14.260(3)$, $b = 16.088(3)$, $c = 17.062(3)$ Å, $\beta = 95.14(3)°$; $V = 3899(1)$ Å^3; $Z = 4$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 48.2°$. 21835 reflections, 6088 independent ($R_{int.} = 0.0747$); $R_1 = 0.549$, $wR_2 = 0.1251$ (based on F^2) for 501 parameters and 3837 refelctions with $I > 2\sigma(I)$. **7**: monoclinic, space group $C2/m$; $a = 13.819(1)$, $b = 19.796(1)$, $c = 45.796(3)$ Å, $\beta = 95.725(1)°$; $V = 12466(1)$ Å^3; $Z = 8$, $Mo_{K\alpha}$ radiation, $2\Theta_{max} = 55.3°$. 34197 reflections, 12836 independent ($R_{int.} = 0.0433$); $R_1 = 0.0508$, $wR_2 = 0.0665$ (based on F^2) for 739 parameters and 9882 reflections with $I > 2\sigma(I)$. **10a**: monoclinic, space group $P2_1/c$; $a = 9.102(5)$, $b = 8.629(5)$, $c = 35.300(20)$ Å, $\beta = 95.93(5)°$; $V = 2757(3)$ Å^3; $Z = 4$, $Cu_{K\alpha}$ radiation, $2\Theta_{max} = 100.0°$. 2829 reflections, 2829 independent ($R_{int.} = 0.0$); $R_1 = 0.0327$, $wR_2 = 0.0910$ (based on F^2) for 290 parameters and 2434 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms in **5b**, **6**, **7** and **10a** were refined with anisotropic, hydrogen atoms at calculated positions with common isotropic parameters (riding model). One CF_3 group in **5b,** and the BF_4^- ion in **6** were refined as rigid bodies on two positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-106557 (**6**), 106559 (**5b**), 106560 (**7**) and 113781 (**10a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). b) ORTEP drawings of the molecular structures of **5b**, **6**, and **7** are available from the author on request.

[12] a) G. Chandra, P. Y. Lo, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1987**, *6*, 191; b) P. B. Hitchcock, M. F. Lappert, N. J. W. Warhurst, *Angew. Chem.* **1991**, *103*, 439; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 438.

Study of the Interactions between Poly(vinyl pyrrolidone) and Sodium Dodecyl Sulfate by Fluorescence Correlation Spectroscopy

Ralf Nörenberg,* Jürgen Klingler, and Dieter Horn

Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Interactions between polymers and surfactants in aqueous solutions are attracting much attention at present as many formulations and industrial processes make simultaneous use of polymers and surfactants for their complementary or even synergistic roles.[1] In many of these applications the optimization of the properties of the polymer in the presence of interference from other chemicals demands a method that is capable of monitoring the association behavior in complex media, in a wide concentration regime, and with less effort than the presently available methods permit. There have been a lot of experimental techniques explored in the past to study the complex formation.[2–6] All of them, however, have their specific limitations. The first method used to study the complex formation was NMR-self-diffusion by monitoring the hydrodynamic size of surfactant molecules.[7] However, this method is limited in the concentration range accessible and also takes a lot of effort.

With the ongoing development of optical correlation techniques, measurements of the self-diffusion coefficient of fluorescing molecules by fluorescence correlation spectroscopy (FCS)[8] became a practical laboratory technique in the last few years.[9] Since fluorescence is a very sensitive technique measurements of the self-diffusion coefficient can be extended to very low concentrations.[10] We present herein the first study of the complex formation of sodium dodecyl sulfate (SDS) with poly(vinyl pyrrolidone) (PVP) by FCS to demonstrate its applicability for associating colloidal systems. The complexes of SDS with PVP belong to the best studied model systems in the literature and often serve as a reference system.

Fluorescence correlation spectroscopy uses fluctuations in the numbers of fluorescent molecules (or particles) in a very small observation volume to obtain information on the diffusive properties of these molecules.[11] The resulting autocorrelation functions $G(t)$ were fitted to the theoretical Equation (1).[10]

$$G(t) = 1 + \frac{1}{N}\left(\frac{1}{1 + \frac{4Dt}{r^2}}\right) \qquad (1)$$

In this equation N is the average number of fluorescent molecules, D the thermal diffusion coefficient of the molecules and r the radial width of the laser focus. The value of r was obtained by calibrating the instrument with the dye Rhodamin 6G, by assuming a diffusion coefficient of this dye of $2.8 \times 10^{-10}\,m^2 s^{-1}$. The diffusion coefficients in this study

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1433-7851/99/3811-1626 $ 17.50+.50/0

were converted into apparent hydrodynamic diameters according to the Einstein equation [Eq. (2)] to give more intuitively accessible results.

$$d = \frac{kT}{3\pi\eta D} \qquad (2)$$

Here d is the hydrodynamic diameter of the diffusing molecule, k the Boltzmann constant, T the absolute temperature, and η the viscosity of the medium. The diameters given below are the average of ten measurements for each sample (typical standard deviation 5%).

It is possible to study a wide range of polymer and surfactant concentrations with FCS. Figure 1 shows the results obtained by monitoring the self-diffusion coefficient of the fluorescence-labeled surfactant molecules in solutions with different concentrations of Kollidon K90 (from 30 $\mathrm{mg\,L^{-1}}$ to 3 $\mathrm{g\,L^{-1}}$). The corresponding curve for pure SDS is shown as a reference.

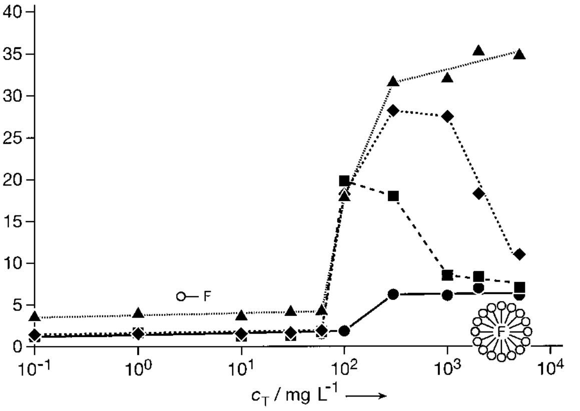

Figure 1. Apparent hydrodynamic size of the fluorescent surfactant SDecS (d_{fl}) as a function of SDS concentration (c_T) for several concentrations of Kollidon K90 ($M_w = 10^6$ Da). Polymer concentration: ● = 0, ■ = 0.03, ◆ = 0.3, ▲ = 3 $\mathrm{g\,L^{-1}}$.

At very low surfactant concentrations the molecules are solubilized by individual solvation shells. In this system the diffusion coefficient of the labeled SDecS molecules is constant and resembles the hydrodynamic size of a single molecule with a diameter of about 1.1 nm. At a concentration of about 300 $\mathrm{mg\,L^{-1}}$ (about 1.0 mM) the apparent size of the labeled surfactant begins to increase steeply up to a new level of about 5 nm. This concentration is about the critical micelle concentration (CMC) of SDS under the applied conditions and coincides with the CMC measured with other techniques, when the salt concentration dependence is accounted for by Equation (3) with $c_{\mathrm{salt}} = 0.5$ M.[12]

$$\ln c_{\mathrm{CMC}} = -7.3 - 0.5 \ln c_{\mathrm{salt}} \qquad (3)$$

In addition, the hydrodynamic size found for the surfactant aggregates at high concentrations is in reasonable agreement with light scattering data. The steepness of the function originates from the highly cooperative nature of the micelle-forming process.

The behavior of the FCS signal changes significantly in the presence of 30 $\mathrm{mg\,L^{-1}}$ PVP in the solution. Again, at low concentrations the size of the fluorescing moiety corresponds to the hydrodynamic size of a single surfactant molecule. At intermediate concentrations, however, a sudden rise in hydrodynamic diameter occurs up to values of about 10 nm. This process occurs at concentrations of 80 $\mathrm{mg\,L^{-1}}$ (0.3 mM surfactant), which is significantly lower than the CMC of the bare molecule and is in accordance with the critical association concentration (CAC) obtained by surface tension measurements.[13] At higher surfactant concentrations the apparent size of the aggregates decreases. We explain this behavior by a saturation of the binding capacity of PVP by the surfactant. Additional surfactant molecules form micelles as in the PVP-free case.

The CAC, identified from the steep increase of the hydrodynamic size, does not change upon increasing the polymer concentration even further to 300 $\mathrm{mg\,L^{-1}}$ and 3 $\mathrm{g\,L^{-1}}$. This result provides clear evidence that the CAC of the system is independent of the polymer concentration, as was shown with fluorescence probe studies.[4a]

We find a different behavior of the dependencies of the hydrodynamic size on the surfactant interaction at the three presented polymer concentrations. At low surfactant concentration the hydrodynamic sizes coincide with the hydrodynamic size of the single surfactant molecule. The increase takes place in a similar fashion. The hydrodynamic sizes differ, however, in the next concentration steps.

A decrease of the hydrodynamic size down to the bare surfactant micelle size appears at low polymer concentration. At intermediate polymer concentration the fall-off is less pronounced and the maximum of the curve reaches a higher size. At the highest polymer concentration studied we find, instead of a fall-off regime, a plateau at a hydrodynamic diameter of 35 nm in the case of Kollidon K90. This value corresponds roughly to the coil diameter of the PVP under these conditions.

If there are a lot of molecules molecularly solvated or bound in bare surfactant micelles, the average value for the hydrodynamic size is lowered. We attribute the above mentioned fall-off process to an increased contribution of small micelles to the average particle size. This picture is sketched in Figure 2.

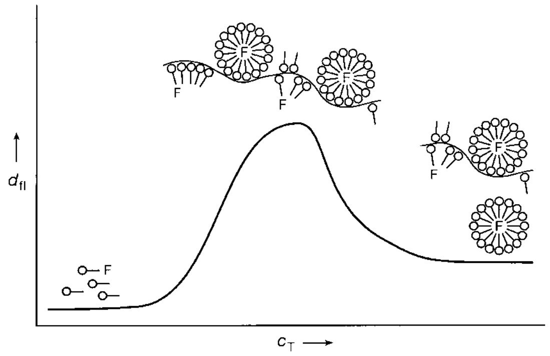

Figure 2. Schematic representation of the interpretation of the hydrodynamic size with the surfactant concentration. At low surfactant concentrations the hydrodynamic size corresponds to a free surfactant molecule. The curve bends at the CAC of the complex. The hydrodynamic size increases as a consequence of an increased contribution of polymer-bound surfactants until the maximum surfactant load of the polymer is reached. The decrease is attributed to the increased contribution of pure surfactant micelles.

As in the case of NMR self-diffusion, one can calculate the measured diffusion coefficient by a weighted sum over the individual diffusion coefficients D_{free}, D_{micelle}, and D_{mm} for the surfactant molecules that are free, bound in surfactant micelles, and in mixed polymer–surfactant micelles, respectively [Eq. (4)].[14]

$$D_{\mathrm{obs}} = w_{\mathrm{free}} D_{\mathrm{free}} + w_{\mathrm{micelle}} D_{\mathrm{micelle}} + w_{\mathrm{mm}} D_{\mathrm{mm}} \qquad (4)$$

Equation (4) can be fitted to the titration curves to yield the relative amounts of free, micelle-bound, and polymer-bound surfactant molecules. Figure 3 shows analogous data for the shorter chain PVP ($M_w = 5 \times 10^4$ Da). This Figure also includes the curve for the pure surfactant as a reference. A sudden increase in particle size at concentrations well below the CMC of the pure surfactant is again observed on adding polymer to the solution. This critical surfactant concentration is the same as with the higher M_w PVP discussed above. The other features of the results are similar, too: For all polymer concentrations studied we find the same CAC of about 80 mg L^{-1} surfactant. At a polymer concentration of 30 mg L^{-1} the formation of a weak maximum in the size is observed. This result is a consequence of the formation of the PVP complex with the SDS micelles. At higher surfactant concentrations the detected size of the fluorescent probe decreases to the value of the bare micelles. Here again the argument holds that at a certain concentration of SDS the polymer is saturated in its micelle-binding capacity and additional surfactant forms small micelles that contribute significantly to the overall signal. At higher polymer concentrations a plateau in the apparent miscelle size of 12 nm is observed, which correlates well with the hydrodynamic size of the polymer.

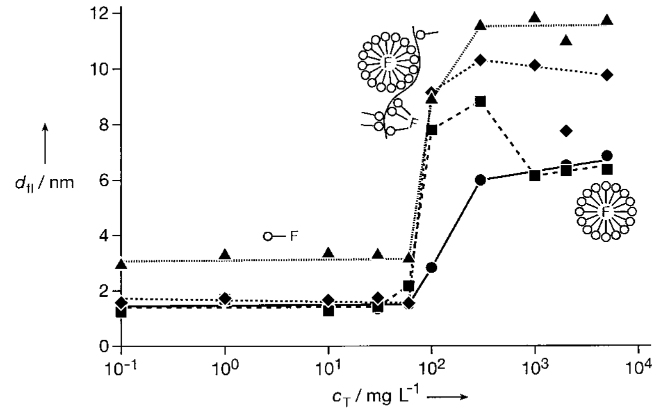

Figure 3. Apparent hydrodynamic size of the fluorescent surfactant SDecS (d_{fl}) as a function of SDS concentration (c_T) for several concentrations of Kollidon K30 ($M_w = 5 \times 10^4$ Da). Polymer concentration: ● = 0, ■ = 0.03, ◆ = 0.3, ▲ = 3 g L^{-1}.

In all cases, either with the high molecular weight or with the low molecular weight polymer, we find maxima, which allow us to calculate the composition of the PVP–SDS complex at saturation. From the corresponding concentrations we find a saturation value of about 3.3 g SDS per gram of PVP for all polymer concentrations and types. Murata et al. report a value of 3.4 g SDS per gram of PVP from a binding isotherm determination.[12]

The measurements presented here show the first application of FCS for the study of polymer–surfactant interactions. The experiments described herein show the formation of micelles and mixed polymer–surfactant micelles on a molecular level. In contrast to other methods, these measurements can be performed in a very dilute solution. Under these conditions viscosity effects arising from interacting polymer tails and chains and charge interactions between two anionically loaded PVP molecules do not have to be considered. We observe the CAC of the system to be 80 mg L^{-1} surfactant, and independent of the size and concentration of the PVP. The presence of a maximum in the size versus surfactant concentration profile indicates that there is an upper limit for the amount of surfactant micelles that can be accommodated by PVP. The further use and development of this technique will include the application to more complex systems.

Experimental Section

We used two samples of technical poly(vinyl pyrrolidone) (BASF) with average molecular weight $M_w = 10^6$ Da (Kollidon K90, K value (viscosity measurement) 90) and $M_w = 5 \times 10^4$ Da (Kollidon K30, K value 30). The fluorescent probe was a terminally fluorescence labeled SDecS that is analogous to SDS in its formation of micelles and surface active properties (Molecular Probes Ltd., catalogue No. D-3829) used at 10 nM (0.005 mg L^{-1}) in a mixture with normal SDS (Aldrich). All chemicals were used as obtained without further purification.

The experiments were performed on a commercial FCS apparatus (ConfoCor, Carl Zeiss Jena; illumination: 488 nm; water immersion objective: 63 ×, 1.2 NA; detection pinhole: 45 nm). The fluorescence correlation function of each sample was measured ten times with a measurement duration of 60 s each. The experiments were carried out in 0.5 M NaCl solution (filtered through a 0.2 μm filter) at 24 °C. All solutions were equilibrated after preparation for at least 1 h before measurement. No change of FCS results between 1 h and 24 h after preparation of the samples was observed.

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[1] E. D. Goddard in *Interactions of Surfactants with Polymers and Proteins* (Eds.: E. D. Goddard, K. P. Ananthapadmanabhan), CRC, Boca Raton, FL, **1993**.

[2] For reviews, see a) E. D. Goddard, *Coll. Surf.* **1986**, *19*, 255–300; b) E. D. Goddard, in *Surfactants in solution*, *Vol 11* (Eds.: K. L. Mittal, D. O. Shaw) Plenum, New York, **1991**, 219–242.

[3] E. D. Goddard, R. B. Hannan, *J. Am. Oil Chem. Soc.* **1977**, *54*, 561–566.

[4] a) R. Zana, J. Lang, P. Llanos, *Polym. Prep. (Am. Chem. Soc Div. Polym. Chem.)* **1982**, *23*, 39–40; b) J. van Stam, M. Almgren, C. Lindblad, *Prog. Colloid Polym. Sci.* **1991**, *84*, 13–20; c) K. Thalberg, J. van Stam, C. Lindblad, M. Almgren, B. Lindman, *J. Phys. Chem.* **1991**, *95*, 8975–8982.

[5] H. Hoffmann, *Tenside Surfactants Deterg.* **1995**, *32*, 462–469.

[6] S. Panmai, R. K. Prud'homme, D. G. Peiffer, S. Jockusch, N. J. Turro, *Polym. Mater. Sci. Eng.* **1998**, *79*, 419–420.

[7] A. Carlsson, G. Karlström, B. Lindman, *J. Phys. Chem.* **1989**, *93*, 3673–3677.

[8] D. Magde, E. Elson, W. W. Webb, *Phys. Rev. Lett.* **1972**, *29*, 705–708.

[9] R. Rigler, Ü. Mets, J. Widengren, P. Kask, *Eur. Biophys. J.* **1993**, *22*, 169–175.
[10] D. Horn, J. Klingler, W. Schrof, K. Graf, *Progr. Colloid Polym. Sci.* **1998** *111*, 27–33.
[11] R. Rigler, J. Widengren, Ü. Mets, in *Fluorescence Spectroscopy* (Ed.: O. Wolfbeis), Springer, Berlin, **1993**.
[12] M. Murata, H. Arai, *J. Colloid. Interf. Sci.* **1973**, *44*, 475
[13] H. Lange, *Kolloid Z. Z. Polym.* **1971**, *243*, 101.
[14] Strictly speaking, this calculation is only valid for fast exchange (ca. 1 ms) between the bound and the free surfactant fraction on the timescale of the correlation function. For slow exchange, the autocorrelation function [Eq. (1)] will consist of two components with different diffusion coefficients. No significant deviation from Equation (1) was observed in our experiments, however.

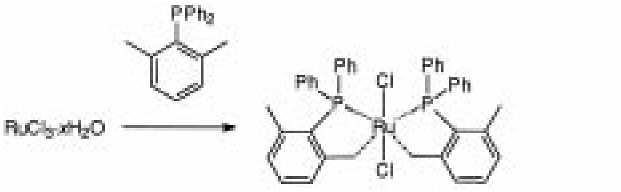
$[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$: A Neutral 14-Electron Ruthenium(II) Complex with Two Agostic Interactions**

Walter Baratta,* Eberhardt Herdtweck, and Pierluigi Rigo

Coordinatively unsaturated transition metal complexes, which play a key role in many catalytic processes, have been often obtained with bulky tertiary phosphanes (PR_3) as ligands that provide steric protection to the empty coordination sites at the metal. The steric crowding forces the R group of the ligand in close proximity to the metal center to induce an agostic interaction[1] between a C–H bond in the R group and the metal atom, thus preventing dimerization or solvent coordination. Ruthenium(II) complexes with small phosphanes are generally six-coordinate 18-electron species of the type $[RuX_2(PR_3)_4]$ (X = halide), whereas with the bulky triarylphosphanes five-coordinate 16-electron complexes such as $[RuCl_2(PPh_3)_3]$ are formed.[2] La Placa and Ibers noted that the close approach of one *ortho*-phenyl hydrogen atom to the metal effectively blocks a coordination site at the ruthenium center.[3] It can be anticipated that when the *ortho*-hydrogen atom of the phenyl rings of PPh_3 are substituted with methyl groups, stronger contacts would occur; the CH_3 group is forced close to metal center, and an agostic interaction is favored. With this in mind, we have been investigating ruthenium(II) complexes with *ortho*-methyl-substituted arylphosphane ligands.

We report herein the isolation and characterization in solution and in the solid state of the formally four-coordinate complex $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$ (**1**), in which the two empty coordination sites on the metal are occupied by one of the methyl groups of each xylyl substituent. No neutral monomeric bis-phosphane 14-electron species have been reported until now, the complexes of stoichiometry $[RuCl_2(PR_3)_2]$ (R = Ph, 3-$C_6H_4SO_3H$)[4, 5] being binuclear derivatives with Ru(μ-Cl)Ru bridges. Recently, the dihydrogen complexes $[RuXX'(H_2)L_2]$ (X, X' = halogen, H; L = P*i*Pr_3, P*t*Bu_2Me) have been used as suitable sources of 14-electron complexes $[RuXX'L_2]$ for the preparation of ruthenium(II) carbene and vinylidene derivatives.[6] Complex **1** is the first example of a neutral ruthenium complex with two agostic interactions, and it can be compared with the recently reported cationic complex $[Ru(Ph)(CO)(PtBu_2Me)_2]^+[BAr'_4]^-$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$).[7]

Reaction of ruthenium trichloride hydrate with a threefold molar amount of (2,6-dimethylphenyl)diphenylphosphane in refluxing methanol afforded the purple, diamagnetic ruthenium complex **1** in good yield [Eq. (a)]. Compound **1** is thermally stable in solution for many hours at room temperature if no air is admitted. The $^{31}P\{^1H\}$ NMR spectra of **1** in different solvents and at different temperatures show only one sharp signal. Therefore, solvent coordination to the ruthenium center or formation of dimeric complexes of the type $[Ru_2Cl_2(\mu\text{-}Cl)_2(PR_3)_4]$ (R = Ph, 3-$C_6H_4SO_3H$),[4, 5] having two nonequivalent phosphane ligands, can be excluded. Moreover, the temperature dependence of the ^1H NMR spectra shows the fluxional behavior of **1** in solution. In fact, above 50 °C the resonances of the methyl protons appear as a broad signal ($\delta = 1.92$ in $C_2Cl_4D_2$ at 80 °C). Upon lowering of the temperature the signal splits into two broad resonances of equal intensity ($\delta = 2.37$ and 1.37 in $C_2Cl_4D_2$ at 20 °C), indicating that the xylyl rotation is slow on the ^1H NMR time scale. Furthermore, below −40 °C the resonance at $\delta = 1.37$ becomes sharp, while that at $\delta = 2.37$ splits into a doublet ($J(H,P) = 5.1$ Hz). Consequently the low-field signal can be attributed to the protons of the methyl group close to the ruthenium atom that couple with one phosphane phosphorus atom. No further splitting of this signal was observed even at −90 °C, so rotation of the interacting CH_3 group cannot be frozen out. The $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ at 20 °C shows two nonbinomial quintets for the *ipso*-carbon atoms of the xylyl and the phenyl groups at $\delta = 134.5$ and $\delta = 132.0$, respectively, which are in agreement with a *cis* arrangement of the two phosphane ligands.[8] At room temperature the spectrum of **1** exhibits two broad signals for the methyl carbon atoms at $\delta = 23.7$ and 11.7. Whereas the first resonance becomes sharp below −20 °C, and is therefore assigned to the noninteracting methyl groups (CH_3 of the free phosphane:



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