the vibronically induced electric dipole (Herzberg–Teller coupling) appears to dominate the parity-forbidden transitions *as well as* the transitions allowed through a static single-ion mechanism. Spin–orbit coupling significantly perturbs the electronic energy levels and redistributes the Z-polarized intensity. For example, the $\Phi_3^B \leftarrow \Phi_3^A$ transition is nominally XY allowed as a one-electron $e_u \leftarrow b_{2g}$ excitation but is in fact predominantly Z polarized.

The same theoretical model has been applied to the Creutz–Taube ion.[7] Unfortunately, in that case only one electronic state of the ($^1A_1 \times {}^2T_2$) multiplet has been clearly identified. Furthermore, the MCD does not follow the absorption profile as closely as in the present case. It seems likely that the vibronically induced electric dipole gives a larger contribution in the Creutz–Taube ion. In the absence of a detailed analysis of the vibronically induced contribution to the absorption and MCD intensities there seems to be no compelling reason to invoke the breakdown of the BO approximation in the Creutz–Taube ion.

A more sensitive test for the breakdown of the BO approximation in both the title and Creutz–Taube complex would be the detection of the so-called "tunneling" transitions in the IR region. This phenomenon is beyond the scope of our current model. The PKS model[4,17] extended to include spin–orbit coupling and all the electronic states of the $^2T_2$ multiplet would have application.

Communications to the Editor

Homoleptic Carbene Complexes. 3. Hexakis(oxazolidin-2-ylidene)cobalt(III) and -rhodium(III)[1]

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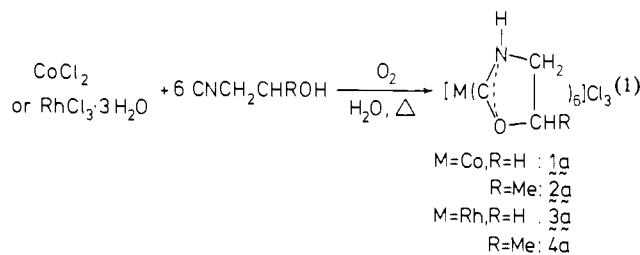der Freien Universität Berlin
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Following Fischer's discovery of the first member in 1964, several hundreds of transition-metal carbene complexes have been reported of which, however, few contained more than one carbene ligand per metal atom, and exceedingly few were homoleptic.[2,3] The question arises, whether this reflects an inherent lability of the metal carbene moiety which is overcome by the presence of stabilizing other ligands or, simply, the lack of appropriate synthetic procedures. Undoubtedly, the most promising one in this respect is nucleophilic addition to metal-coordinated isocyanides which, after all, gave the unique tetracarbene palladium and platinum species.[4] There are, however, certain requirements such as the existence of the parent homoleptic isocyanide complexes and a sufficiently high reactivity of all four (or even six) isocyanide ligands, which are barely met.

We wish to demonstrate here that the situation becomes much more favorable if functional isocyanides of the type CNCHRCHR'OH are employed, which contain both the isocyano group and the nucleophile in the same molecule, giving access for the first time to *hexacarbene complexes.*

The reactions between metal chloride and 2-hydroxyalkyl isocyanide were carried out in warm ethanol or water. Air was passed through the solution with the intent of oxidizing cobalt(II) and in anticipation that this would prevent rhodium(III) from being reduced by the isocyanide. Concentration of the solution followed by addition of acetone caused precipitation of **1a–4a** as

white solids (eq 1). Recrystallization from hot alcohol or water

$$\text{CoCl}_2 \text{ or RhCl}_3\cdot 3\text{H}_2\text{O} + 6\text{ CNCH}_2\text{CHROH} \xrightarrow[\text{H}_2\text{O, }\Delta]{\text{O}_2} [\text{M(C}{\overset{\text{N—CH}_2}{\underset{\text{O—CHR}}{|}}})_6]\text{Cl}_3 \quad (1)$$

M=Co,R=H : **1a**
R=Me: **2a**
M=Rh,R=H : **3a**
R=Me: **4a**

gave clear hexagonal prisms in 75–85% yield which, according to microanalysis, contain varying amounts of water. Drying at 80 °C in vacuo produces hygroscopic but otherwise enormously stable material with decomposition points well above 150 °C.

The molar conductivities of 10^{-7} M aqueous solutions of **1a** and **4a** were found to be 295 and 241 ohm⁻¹ cm² mol⁻¹, respectively, which is typical of 3:1 electrolytes.[5] Similar properties are shown by the corresponding PF₆⁻ salts **1b–4b**[6] in acetone and nitromethane solution. With BPh₄⁻ counterions, on the other hand, a product **1c** was obtained which analyzed as bis(tetraphenylborate) and in fact turned out to be a 1:2 electrolyte in nitromethane (Λ_M(22 °C) = 137 ohm⁻¹ cm² mol⁻¹ at 10^{-7} M). According to solid-state susceptibility measurements, however, **1c** is diamagnetic (χ(293 K) = -1.0×10^6 cgsu), which can only be rationalized by assuming a cobalt(III) species of type **1a** with one of the carbene ligands being deprotonated.

Strong IR absorptions (KBr) at 3400–2900 [ν(NH) + ν(CH)], 1550 [ν_a(Nsb3· ·eb3Csb3· ·eb3O)], and 1160 [ν_s(Nsb3· ·eb3C sb3· ·eb3O)] cm⁻¹ as observed in the compounds **1–4** are characteristic of the oxazolidin-2-ylidene ligand as are ¹H NMR features in the 7.5–9.5 (NH) and 3.5–4.5 ppm (ring-CH's [AA'BB' resp.ABX multiplets]) regions.[1] More direct support of (terminal) metal–carbon (carbene) bonding in **1–4** comes from the ¹³C resonances (in D₂O or acetone-d_6) at 200–220 ppm and,

(1) Part 2: Fehlhammer, W. P.; Bartel, K.; Plaia, U.; Völkl, A.; Liu, A. T. *Chem. Ber.*, in press.
(2) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* 1964, *3*, 580.
(3) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Weinheim, 1983.
(4) Miller, J. S.; Balch, A. L. *Inorg. Chem.* 1972, *11*, 2069.

(5) Geary, W. J. *Coord. Chem. Rev.* 1971, *7*, 81.
(6) Typical procedure (**4b**): CNCH₂CHMeOH (0.39 mL, 4.56 mmol) was added to a solution of RhCl₃·3H₂O (0.20 g, 0.76 mmol) in 20 mL of water. After the mixture was warmed to 60 °C, air was bubbled through the mixture for 1 h producing a clear, almost colorless solution to which NH₄PF₆ (0.37 g, 2.28 mmol) was added with stirring. On cooling to room temperature, analytically pure **4b** separated as white crystals (mp 229–232 °C dec) in almost quantitative yield. Anal. Calcd for C₂₄H₄₂F₁₈N₆O₆P₃Rh: C, 27.50; H, 4.04; N, 8.02. Found: C, 27.78; H, 4.10; N, 8.00.

$\lceil Co\{\overline{CNHCH_2CH_2O}\}_5\{\overline{C=NCH_2CH_2O}\}\rceil (BPh_4)_2$
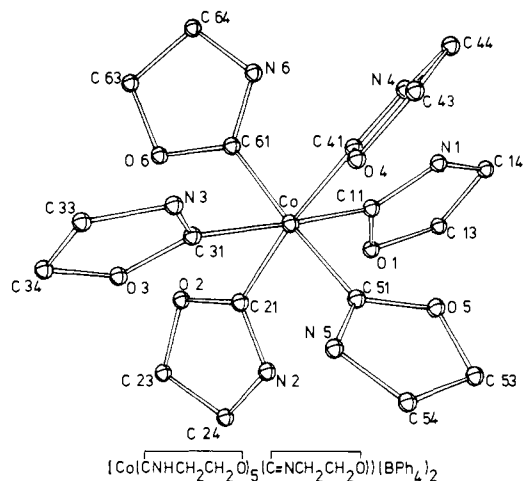
Figure 1. View of the complex cation of **1c**. Atoms have been drawn as spheres of arbitrary radius, hydrogen atoms have been omitted. Averaged bond distances (Å) within heterocycles: C1–O, 1.36 (2); O–C3, 1.49 (2); C3–C4, 1.56 (2); C4–N, 1.51 (2); N–C1, 1.33 (2).

particularly, from the appearance of a well-resolved ^{103}Rh–^{13}C coupling (J = 36 Hz) in the case of **4b**. Similar δ (187.2) and J (35 Hz) values have been reported for [Rh[$\overline{C(NHR)N}$-$\overline{(Me)C(NHR)}$](Me)(I)(CNR)$_2$]$^+$ (R = t-Bu).[7] The UV spectra (e.g., **2a** (H$_2$O) 295 (2.53), 230 (sh), <190 (>4.7) [CT band] nm (log ϵ)) reflect the expected high ligand field splitting capacity of the carbene ligand which even surpasses that of cyanide in hexacyanocobaltate(III)[8] and -rhodate(III).[9]

Conclusive evidence for the existence of hexacarbene complexes is finally produced by an X-ray analysis of **1c**.[10] In spite of the poor quality of the data,[11] the overall geometry of a central cobalt atom surrounded by six five-membered rings is reliably defined (Figure 1) with the average values of the ring dimensions comparing favorably with those determined recently for tetrakis(oxazolidin-2-ylidene)palladium dichloride.[1] In both cases, the metal to carbene distances ($\overline{Co–C}$, 1.95 (1); $\overline{Pd–C}$, 2.020 (2) Å) are only slightly shorter than the estimated M–C$_{sp^2}$ single-bond lengths (Co–C, 1.96; Pd–C, 2.05 Å), precluding any significant metal to carbon π bonding.

In summary, the combination of 2-hydroxyalkyl isocyanides with higher valent metals opens the most efficient route to (particularly homoleptic) carbene complexes[1,12] of which the hexacarbene species **1–4** represent a new genus. Their syntheses, most surprisingly, are best carried out under rather "non-organometallic"-type reaction conditions. Actually, this exemplifies an interesting trend in modern organometallic chemistry away from inert atmospheres, nonpolar solvents, and low oxidation states of metals which has already led to some rather spectacular results.[13–16]

(7) Branson, P. R.; Cable, R. A.; Green, M.; Lloyd, M. K. *J. Chem. Soc., Chem. Commun.* **1974**, 364. Comparison is further indicated with [Rh-(CN)$_6$]$^{3-}$ showing an almost identical *J* (33.6 Hz) but differing considerably in the δ (131.9) value: Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 924.

(8) Kataoka, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2078.

(9) Schmidtke, H. H. *Z. Phys. Chem. Neue Folge* **1964**, *40*, 96.

(10) Crystal data for [Co($\overline{C=NCH_2CH_2O}$)($\overline{CNHCH_2CH_2O}$)$_5$]-(BPh$_4$)$_2$·acetone (**1c**): space group $P2_1/n$; a = 18.016 (3) Å, b = 30.684 (6) Å, c = 11.528 (2) Å, β = 97.89 (2)°; Z = 4, d_{calcd} = 1.24 g cm^{-3}; R = 0.102 for 4246 reflections having $I > 2\sigma(I)$.

(11) A consequence of both considerable crystal decomposition during the data collection and an unresolved disorder of the acetone.

(12) Bartel, K.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599.

(13) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243.

(14) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176.

(15) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383.

(16) Kauffmann, Th.; Fiegenbaum, P.; Wieschollek, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 531.

An Anomalously Long-Wavelength Electronic Transition in Conformationally Locked Organosilane High Polymers

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The first organosilane polymers (i.e., polymers containing only silicon in the backbone) were reported in 1924,[1] but these highly insoluble and intractible materials evoked little scientific interest. Recently, however, the synthesis of soluble substituted polysilane derivatives[2] has both rekindled considerable scientific interest and has spawned the development of a number of new applications.[3]

One of the most intriguing properties of catenated substituted silane derivatives is their remarkable electronic absorption spectra.[4] An intense absorption, described variously as either a $\sigma\sigma^*$ or a $\sigma 3d\pi_{Si-Si}$ transition,[5] moves initially to longer wavelengths with increased silicon catenation but rapidly approaches a limiting value with increasing chain length.[6] For this reason, most simple, alkyl-substituted silane high polymers absorb around 305–320 nm.[4] We report here the surprising observation that this limiting value apparently applies only to polysilane derivatives either in solution or in the amorphous solid state and that in certain cases where conformational rigidity is enforced, for example, by side-chain crystallization, the electronic absorption of the polysilane backbone occurs at considerably longer wavelengths.

In a continuing study of the photolability of substituted silane high polymers as a function of the substituents, we have prepared a number of symmetrically disubstituted polymers by the condensation of the appropriate silyl dichlorides with sodium as shown below.[2d] The electronic absorption spectra of **2a** and **2b** were as expected,[4] showing a strong absorption in the 310–320-nm region both in solution or as solid films. The absorption spectrum of poly(di-*n*-hexylsilane) (PDHS) in the solid state was, however, most unusual.

(1) Kipping, F. S. *J. Chem. Soc.* **1924**, *125*, 2291.

(2) (a) Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polymn. Chem. Ed.* **1980**, *18*, 959. (b) Trujillo, R. E. *J. Organomet. Chem.* **1980**, *198*, C27. (c) West, R.; David, L. D.; Djurovich, P. I.; Stearly, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. (d) Trefonas, P., III; Djurovich, P. I.; Zhang, X. M.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819.

(3) (a) Yajima, S.; Liaw, C. F.; Omori, M.; Hayaski, J. *Chem. Lett.* **1976**, 435. (b) Mazdyasni, K. S.; West, R.; David, L. D. *J. Am. Ceram. Soc.* **1978**, *61*, 504. (c) Yajima, S.; Hasegawa, Y.; Hayashi, Y.; Oimora, M. *J. Mater. Sci.* **1980**, *15*, 720. (d) Schilling, C. L.; Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polymn. Symp.* **1983**, *70*, 121. (e) Hofer, D. C.; Miller, R. D.; Willson, C. G.; Neureuther, A. R. *SPIE Adv. Resist Technol.* **1984**, *469*, 108. (f) Hofer, D. C.; Miller, R. D.; Willson, C. G. *SPIE Adv. Resist Technol.* **1984**, *469*, 16.

(4) Trefonas, P., III; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823 and references cited therein.

(5) (a) Kumada, M.; Tomas, K. *Adv. Organomet. Chem.* **1968**, *6*, 80. (b) Pitt, C. G.; Bursey, M. M.; Rogerson, P. F. *J. Am. Chem. Soc.* **1970**, *92*, 519. (c) Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1974**, *71*, C27. (d) Pitt, C. G. "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; Chapter 8 and references cited therein.

(6) Pitt, C. G.; Jones, L. L.; Ramsey, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471.

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