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Bis(phenylethynyl)hafnocene as an Organometallic Chelate Ligand

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The application of $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2$ (**1**) as an organometallic chelate ligand towards different organometallic building blocks will be discussed. **1** reacts with $Ni(CO)_4$ (**2**) or $Co_2(CO)_8$ (**4**) to yield $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2\}M(CO)$ (M=Ni: **3**, M=Co: **5**) and $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)$ $[\mu\text{-}(\eta^2\text{-}C{\equiv}CPh)\text{-}Co_2(CO)_6]$ (**6**). In **6** one of the two phenylethynyl units is η^2-side-on coordinated to $Co_2(CO)_6$ forming a 1, 2-dicobaltatetrahedrane unit. However, the reaction of **1** with $Fe_2(CO)_9$ (**7**) affords $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf[(\eta^2\text{-}C{\equiv}CPh)Fe(CO)_4]_2$ (**8**), a compound, in which both of the phenylethynyl ligands are η^2-side-on coordinated to $Fe(CO)_4$ complex fragments. All new synthesized compounds have been characterized by analytical and spectroscopic data. Additionally, the structure of **3** was established by X-ray diffraction study.

The η^2-side-on coordination of alkynes plays an important role in many metal catalyzed alkyne reactions.[1] While this coordination type is well documented in many organometallic templates, there is no evidence for the η^2-side-on coordination of simple metal halides. However, this type of compounds shows, for example in the Reppe chemistry, a versatile catalytical reactivity.[2] We have shown previously that by using $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR)_2$ (R=Ph, $SiMe_3$) as an organometallic bidentate chelate ligand and reacting this complex with $Co_2(CO)_8$, $Ni(CO)_4$, M^ICl (M=Cu, Ag) and MCl_2 (M=Fe, Co, Ni), the bimetallic compounds $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR)_2\}ML_n$ (ML_n=Ni(CO), Co(CO), MCl_2, MCl) could be obtained in high yields.[3—6] Their application as homogenous catalysts is currently under investigation.[7] We herein, would like to report the reactivity of the analogous compound $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2$ (**1**) toward organometallic compounds.

Results and Discussion

Bis(phenylethynyl)bis(trimethylsilylcyclopentadienyl)hafnium (**1**) reacts with $Ni(CO)_4$ (**2**) in toluene at 25°C under vigorous CO-elimination to afford the bimetallic complex **3** in an almost quantitative yield (Scheme 1). In **3** the hafnocene compound **1** acts, via its phenylethynyl groups, as a bidentate organometallic chelate ligand (host) to the Ni(CO)-moiety (guest). In order to establish the molecular structure of **3**, an X-ray diffraction study was carried out, the results of which are illustrated in Fig. 1. **3** crystallizes in the monoclinic space group $C2/c$ and shows crystallographic C_2 symmetry; the atoms generated by the C_2 axis (Hf, Ni, C(1), O(1)) are marked with the suffix a. Fig. 1 clearly shows that both of the phenylethynyl ligands in **1** are coordinatively η^2-side-on bonded to the Ni(CO) moiety. The atoms Hf, C(2), C(3), C(9), Ni, C(1), O(1), and also the symmetry related atoms C(2a), C(3a), and C(9a) form exactly a plane. In addition the hafnium-nickel interaction is of interest. The Hf–Ni distance of 296.8 pm in **3** is only slightly longer than that expected for a Hf–Ni single bond.[8] This suggests that there is little, if any, metal-metal interaction. Through the η^2-side-on coordination of the phenylethynyl units in **3** by Ni(CO), the angle C(2)–Hf–C(2a) (87.0°) is considerably reduced in comparison to **1** (99.2°). This leads to a deformation of the Hf–C≡C–Ph unit, which shows an almost linear structure in the non-coordinated state.[9] The observed bond lengthening of the CC-triple bond via the η^2-side-on coordination of the phenylethynyl ligands to Ni(CO), from 119 pm in **1** to 125.0 pm in **3**, is additionally confirmed by IR spectroscopy. The observed absorption of the C≡C-stretching vibration is shifted from 2080 cm^{-1} in **1** to 1880 cm^{-1} in **3**.

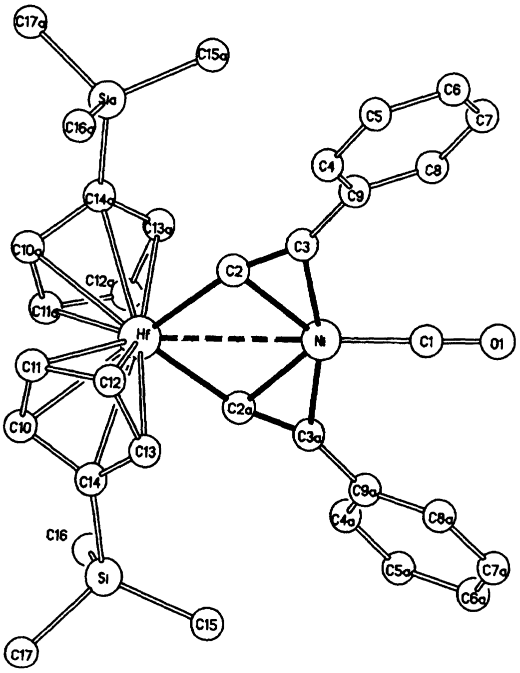
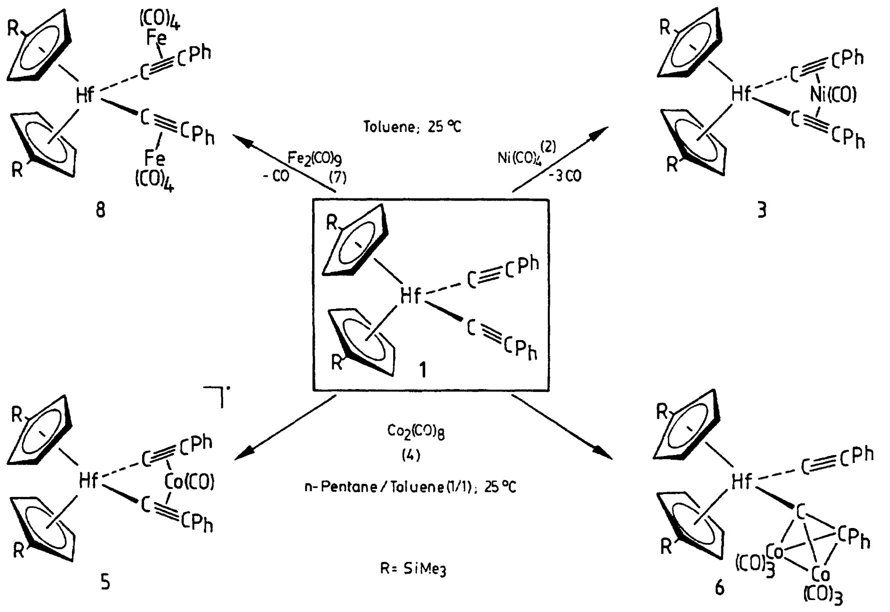


Fig. 1. Molecular geometry and atom labelling scheme for **3**. Selected bond distances (pm) and angles (deg): Hf–Ni 296.8(1), Hf–C(2) 217.0(4), C(2)–C(3) 125.0(5), Ni–C(2) 204.3(4), Ni–C(3) 202.6(4), Ni–C(1) 173.6(7), C(2)–Hf–C(2a) 87.0(2), Hf–C(2)–C(3) 160.7(3), C(2)–C(3)–C(9) 153.0(4), Hf–C(2)–Ni 89.5(1), C(2)–C(3)–Ni 72.8(2), C(1)–Ni–Hf 180(0).

A similar compound, **5**, was obtained as black crys-



Scheme 1. Reaction behavior of $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2$ (**1**) with different organometallic compounds.

tals from the reaction of **1** with equimolar amounts of $Co_2(CO)_8$ (**4**) in toluene at 25°C (Scheme 1). Column chromatography of the reaction mixture through Celite affords two fractions, first **5** and then a second compound (**6**), which could be isolated in good yields. The analytical and spectroscopic data (IR, MS) confirm structures **5** and **6** unequivocally (Scheme 1). **5** was shown to be isostructural with $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2\}Ni(CO)$ (**3**). That both of the two carbon-carbon triple bonds in **5** are η^2-side-on bonded to Co(CO) is indicated in the IR spectrum: **1** shows its $\nu_{C\equiv C}$ absorption at 2080 cm^{-1}, whereas in **5** it is shifted to 1872 cm^{-1}. The same effect was already observed by changing from **1** to **3** (see above). However the analysis of the infrared spectrum of **6** in the carbonyl region shows four ν_{CO} frequencies at 2095, 2058, 2032, and 2028 cm^{-1}, which are typical for $Co_2(CO)_6(RC_2R')$ complexes.[10] That indeed only one of the two phenylethynyl ligands in **6** is η^2-side-on coordinated to $Co_2(CO)_6$ is given by the observation of an absorption at 2078 cm^{-1}, which can be assigned to a non-coordinated CC-triple bond.

The assumption that the three ligands (two C≡C and one CO) around the cobalt atom each contribute two electrons and that the cobalt atom itself contributes nine electrons to the total electron count of the "$(C{\equiv}C)_2Co(CO)$" fragment, implies that this unit acts as a 15-electron complex fragment. The magnetic moment μ_{eff} of **5** was found to be 3.9 B.M. and confirms that this dinuclear compound is indeed paramagnetic and contains a total of three unpaired electrons.

Treatment of **1** with 2.5 equivalents $Fe_2(CO)_9$ (**7**) in toluene at 25°C yields complex **8** (Scheme 1). The characterization of **8** is based on analytical and spectroscopic data, which are given in the experimental part. The formulation of **8** as a compound in which each of the two phenylethynyl ligands is η^2-side-on coordinated to the 16-electron complex fragment $Fe(CO)_4$ is consistent with the IR and FD-mass spectrum of **8**. The application of compounds **3** and **5** as catalysts in homogeneous catalysis is under investigation,[7] as well as the reactivity of **1** with element(I) and element(II) salts of Fe^{II}, Ni^{II}, and Cu^{I}, Ag^{I} compounds.

Experimental

General Comments. All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques.

A) Synthesis of 3: To 1.0 g (1.53 mmol) **1**[11] dissolved in 200 ml toluene at 25°C was added an equimolar amount of $Ni(CO)_4$ (**2**) in one portion. The reaction mixture gradually turned deep yellow. After it had been stirred at 25°C for 5 h the solvent was evaporated under high vacuum and the resulting orange-red residue was filtered with pentane through Celite (10×2.5 cm). Evaporation of pentane under reduced pressure gave 1.1 g (1.48 mmol) of **3** as a dark orange crystalline solid in 97% yield. Recrystallization from pentane at −30°C gave pure material; mp 142°C. Found: C, 53.76; H, 4.89%. Calcd for $C_{33}H_{36}HfNiOSi_2$: C, 53.41; H, 4.83%. IR (pentane, CaF_2 cells) ν=2009(vs) [$\nu_{(CO)}$], ν=1880(w) cm^{-1} [$\nu_{(C\equiv C)}$]; ^1H NMR ($CDCl_3$) δ=0.27 (s, 18 H, $SiMe_3$), 5.53 (t, 8H, J_{HH}=2.3 Hz, $C_5H_4SiMe_3$), 5.99 (t, 8H, J_{HH}=2.3 Hz, $C_5H_4SiMe_3$), 7.3—7.8 (m, 10H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=0.5 (s, 6C, $SiMe_3$), 108.2 (s, 4C, $C_5H_4SiMe_3$), 111.4 (s, 4C, $C_5H_4SiMe_3$), 115.0 (s, 2C, $^iC/C_5H_4SiMe_3$), 122.3 (s, 2C, ^iC/Ph), 127.3 (s, 2C, Ph), 127.8 (s, 2C, C≡C), 128.5 (s, 4C, Ph), 130.8 (S, 4C, Ph), 174.5 (s, 2C, C≡C), 200.0 (s, 1C, CO); FD-MS m/z=742 [M^+].

Single crystals of **3** were grown from a saturated toluene/pentane solution at −50°C. A crystal of dimensions 0.25×0.2×0.2 mm was secured in a glass capillary and sealed under nitrogen. Compound **3** crystallizes in the monoclinic space group $C2/c$ with lattice constants a=2192.6(6), b=

1066.6(3), $c=1348.1(4)$ pm, $\beta=98.53(2)^\circ$, $V=3117(1)\times10^6$ pm^3, $Z=4$, $\mu(\mathrm{Mo}\,K_\alpha=4.4\ \mathrm{cm}^{-1})$. Diffraction data were collected on a Nicolet (Siemens) R3 diffractometer by using the θ–2θ technique (2θ limits $2^\circ\leqslant2\theta\leqslant48^\circ$, scan-range 0.75°, scan-speed $2.9\leqslant\dot{\omega}\leqslant24.3$ deg min^{-1} and Mo K_α radiation ($\lambda=71.069$ pm) at 223 K. The structure was solved by direct methods (SHELXTL-PLUS)[12] on 2282 unique reflections with $F\geqslant4\sigma(F)$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions. An empirical absorption correction was applied. The final discrepancy indices were $R_f=2.18\%$ and $R_w=2.06\%$. A complete list of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structure factors have been deposited as Document No. 66001 at the Office of the Editor of Bull. Chem. Soc. Jpn.

B) Synthesis of 5 and 6: To 600 mg (0.92 mmol) of **1** dissolved in 100 ml toluene was added dropwise an equimolar amount of $Co_2(CO)_8$ (**4**) dissolved in 50 ml toluene/pentane (1/1) at 25°C. Workup similar to that described earlier, followed by column chromatography at −30°C (column size: 30×2.5 cm; Celite; pentane) yielded first with pentane/toluene (10/1—5/1) a red-brown (**5**) and then with pentane/toluene (5/1—1/1) a deep red (**6**) fraction. Evaporation of the solvents at reduced pressure and recrystallization from pentane/toluene at −30°C gave pure 100 mg (0.135 mmol) (22%) of **5**[9] and 280 mg (0.297 mmol) (50%) of **6**.

6: Mp 168°C (decomp). Found: C, 48.82; H, 3.78%. Calcd for $C_{38}H_{36}O_6Co_2HfSi_2$: C, 48.49; H, 3.86%. IR (CH_2Cl_2; CaF_2 cells): $\nu=2095$ (m), 2058 (vs), 2032 (vs), 2028 (vs) [$\nu_{(CO)}$]; $\nu=2078$ (m) cm^{-1} [$\nu_{(C\equiv C)}$]; ^{1}H NMR ($CDCl_3$) $\delta=0.31$ (s, 18H, SiMe$_3$), 6.34 (m, 8H, $C_5H_4SiMe_3$), 6.41 (m, 8H, $C_5H_4SiMe_3$), 7.1—7.6 (m, 10H, Ph).

C) Synthesis of 8: To 1.0 g (1.53 mmol) **1** in 100 ml toluene were added in one portion 2.5 equivalents of $Fe_2(CO)_9$ at 25°C. Workup similar to that described earlier yielded only dark red **8** in 79% yield (1.20 g, 1.21 mmol); mp 66°C (decomp). Found: C, 47.58; H, 3.92%. Calcd for $C_{40}H_{36}O_8Fe_2HfSi_2$: C, 48.48; H, 3.66%. IR (CH_2Cl_2, CaF_2 cells) $\nu=2071$ (w), 2034 (s), 2011 (vs), 2006 (s) cm^{-1} [$\nu_{(CO)}$]; ^{1}H NMR ($CDCl_3$) $\delta=0.35$ (s, 18H, SiMe$_3$), 6.36 (m, 8H, $C_5H_4SiMe_3$), 6.42 (m, 8H, $C_5H_4SiMe_3$), 7.4 (m, 10H, Ph); FD-MS $m/z=991$ [M$^+$].

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