

SUPPORTED CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES

III *. SILICA-GEL-SUPPORTED IRON AND COBALT DERIVATIVES

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Summary

Mononuclear cyclopentadienylcobalt carbonyl and cyclopentadienyliron carbonyl derivatives were covalently linked to a silica gel support either by reaction of $(C_2H_5O)Si(CH_3)_2C_5H_5$ or of $(C_2H_5O)_3SiC_5H_5$ with macroporous silica gel supported materials and subsequent treatment with $Co_2(CO)_8$ or $Fe_2(CO)_9$, or by reaction of $(C_2H_5O)Si(CH_3)_2C_5H_4Co(CO)_2$ and $(C_2H_5O)_3SiC_5H_4Co(CO)_2$ with a silica gel support. In contrast to their unsupported analogues, no binuclear or polynuclear species are formed from the SiO_2 -supported metal carbonyl derivatives even at temperatures up to $200^\circ C$. The cobalt derivative was found to be a catalyst for olefin hydroformylation reactions.

Binuclear SiO_2 -supported species are formed when $[(C_2H_5O)Si(CH_3)_2C_5H_4Fe(CO)_2]_2$ or $[(C_2H_5O)_3SiC_5H_4Fe(CO)_2]_2$ are treated with a silica gel support. A large fraction of these surface-bound dimers are irreversibly converted into mononuclear hydridoiron carbonyl derivatives by hydrogen at elevated pressures.

Introduction

As support systems for organometallic catalysts, organic and inorganic support materials each offer specific advantages. Organic polymers, such as cross-linked polystyrenes, provide a fairly well-defined environment for organometallic species attached to their surface [2]; silica gel surfaces on the other hand, while less exactly characterized in terms of their structure and reactivity offer distinct advantages in chemical inertness and thermal stability [3]. It therefore seemed of interest to investigate the synthetic methods available for attachment to silica gel surfaces of organometallic moieties and the structural characteris-

* Previous communications: ref. 1, for part II see ref. 1b.

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tics of the resulting surface compounds. In this paper, we describe the synthesis and characterization of SiO_2 -bound cyclopentadienyl-cobalt and -iron carbonyl derivatives.

Results and discussion

Method A. One synthetic route to SiO_2 -bound cyclopentadienylmetal carbonyl compounds involves condensation of functionally-substituted cyclopentadienylsilanes with reactive SiOH groups on the SiO_2 surface [4] and subsequent reaction with a metal carbonyl. Following this approach, ethoxydimethylcyclopentadienylsilane, $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$, or triethoxycyclopentadienylsilane, $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$, were treated in toluene at 80°C with a macroporous, large-surface ($300\text{ m}^2/\text{g}$) silica gel. Carbon analyses indicate that the reaction with $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$ and with $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ introduced ca. $0.4\text{ mmol SiC}_5\text{H}_5/\text{g SiO}_2$ and ca. $0.6\text{ mmol SiC}_5\text{H}_5/\text{g SiO}_2$, respectively. These degrees of functionalisation are reasonable when compared to a density of about $0.65\text{ mmol reactive OH groups per g SiO}_2$, corresponding to $1.4\text{ OH groups per }100\text{ \AA}^2$ [5]. IR absorptions between 2900 and 3000 cm^{-1} are in accord with the presence of vinyl- and alkyl-hydrocarbon moieties. In the formation of $\text{Si}-\text{O}-\text{SiC}_5\text{H}_5$ linkages, $\text{C}_2\text{H}_5\text{OH}$ is released. When $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ was treated with silica gel, diethyl ether was also observed among the products by gas chromatography. This would indicate that some of the cyclopentadienylsilane groups might not only be bound to the surface directly, but also to each other by $\text{Si}-\text{O}-\text{Si}$ linkages. Treatment of these SiO_2 -bound products with aqueous HCl reduces the carbon content only by a small amount (ca. 15%); ethanol is liberated in this reaction, indicating the presence of some residual $\text{C}_2\text{H}_5\text{OSi}$ groups among the surface condensation products*.

Subsequent reaction of these materials with $\text{Co}_2(\text{CO})_8$ in methylene chloride or with $\text{Fe}_2(\text{CO})_9$ in tetrahydrofuran (THF) yields the SiO_2 -bound analogues of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ and $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$. The identification of these materials, both of which have a brown-red colour similar to that of their homogeneous counterparts, is primarily based on their IR absorption bands. The cobalt carbonyl derivatives have absorptions at 2028 and 1967 cm^{-1} , in close agreement with those of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ [6]. Treatment of these materials with I_2 in refluxing diethyl ether affords a monocarbonyl diiodine derivative with one CO -absorption at 2065 cm^{-1} , virtually identical with that of $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})\text{I}_2$ [7]. The hydridoiron carbonyl derivative has the expected $\nu(\text{CO})$ absorptions at 2030 and 1960 cm^{-1} ; the relatively weak $\text{Fe}-\text{H}$ absorption is not clearly discernible from background absorptions in these materials.

Cobalt analyses yield values of ca. 0.3 and $0.5\text{ mmol Co/g SiO}_2$ for $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$ - and $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ -treated silicagel, respectively. These data are in accord with the assumption that most of the cyclopentadienyl groups had reacted to form the cobalt carbonyl derivatives; the possibility cannot be excluded, however, that other cobalt-containing species are deposited on the support material along with the expected silylcyclopentadienylcobalt dicarbonyl. The corresponding data for the iron carbonyl derivatives are $0.25-0.3\text{ mmol Fe/g}$

* IR spectra related to this question have been reported by Hertl [15].

TABLE I
IR ABSORPTIONS IN THE $\nu(\text{CO})$ ABSORPTION RANGE (in cm^{-1})

Derivative	$\nu(\text{CO})$ (cm^{-1})	
	R = SiO_2 -bound $\text{OSi}(\text{CH}_3)_2$ or $\text{OSi}(\text{OC}_2\text{H}_5)_2$ (in nujol mull)	R = H
$\text{RC}_5\text{H}_4\text{Co}(\text{CO})_2$	2020	2028 ^a
	1965	1967
$\text{RC}_5\text{H}_4\text{CoI}_2(\text{CO})$	2070	2068 ^b
$\text{RC}_5\text{H}_4\text{FeH}(\text{CO})_2$	2030	2014 ^c
	1960	1960
$\text{RC}_5\text{H}_4\text{FeI}(\text{CO})_2$	2045	2044 ^d
	1995	2000
$(\text{RC}_5\text{H}_4\text{Fe}(\text{CO})_2)_2$	2003	2000 ^e
	1960	1958
	1795	1786

^a In CHCl_3 [6]. ^b In halocarbon oil mull [7]. ^c In CS_2 [8]. ^d In CHCl_3 [12]. ^e In cyclohexane, data are for $\text{R} = (\text{CH}_3)_3\text{Si}$ [10].

SeO_2 , indicating a conversion of about one half of the cyclopentadienyl groups present into the hydridoiron dicarbonyl derivative.

Method B. An alternative approach to SiO_2 -supported cyclopentadienylmetal carbonyl compounds consists in the synthesis of suitably functionalized cyclopentadienylmetal carbonyl silanes and their subsequent attachment to a silica gel support. Along these lines, $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4\text{Co}(\text{CO})_2$ and $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{C}_5\text{H}_4\text{Co}(\text{CO})_2$ were synthesized by treatment of the corresponding cyclopentadienylsilanes with $\text{Co}_2(\text{CO})_8$ in refluxing methylene chloride. The oily products obtained in this manner were characterized by their mass spectra and IR absorption data; these data indicate that only small amounts of unreacted $\text{Co}_2(\text{CO})_8$ are present in these materials*.

Each of these compounds was then heated together with a macroporous SiO_2 -support material in toluene at 80°C . The products were virtually identical in their spectral properties and elemental analysis data with the corresponding compounds synthesized as described under Method A, except for a somewhat stronger colour and stronger IR absorption in the CO stretching range.

In their reaction behaviour, the SiO_2 -supported cyclopentadienyl-iron and -cobalt dicarbonyl compounds parallel that of their polystyrene-supported counterparts [1]: The SiO_2 -supported silylcyclopentadienylhydridoiron dicarbonyl is completely resistant towards thermal H_2 elimination, and no formation of binuclear iron carbonyl species can be detected in the IR spectra of these materials even after heating to about 180 – 200°C . Similarly, UV irradiation of the SiO_2 -supported silylcyclopentadienylcobalt dicarbonyl derivatives leads to photoelimination of CO ligands without any spectral indication of the formation of binuclear cobalt carbonyl derivatives comparable to those formed in

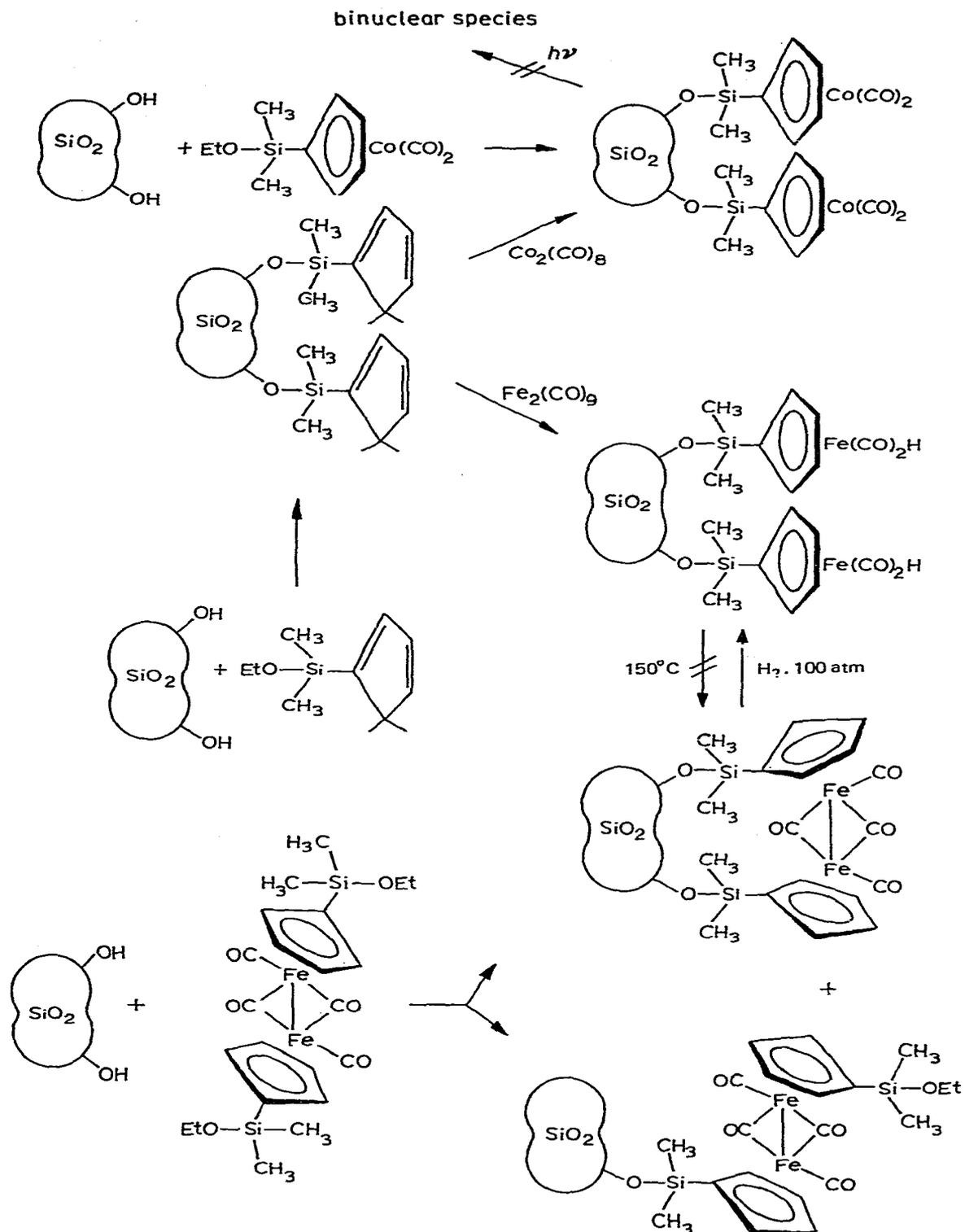
* Because of their oily nature and their reactivity towards oxidic support materials, these compounds could not be further purified by crystallization or chromatography. They may contain some uncomplexed cyclopentadienylsilane. As far as we can determine, such an admixture would not interfere with the subsequent reactions.

homogeneous solution. Thus SiO_2 appears to be equally as effective as the previously described polystyrene supports [1], in inducing and maintaining a mononuclear distribution of the cyclopentadienyl-bound iron and cobalt centers on the surface, as one would expect from a statistical density of roughly 0.4 cyclopentadienylmetal units per 100 \AA^2 of SiO_2 surface.

The cobalt derivatives thus obtained, as well as their polystyrene-supported analogues, catalyze the hydroformylation of olefins in toluene solution between 100 and 150°C . A more detailed analysis of these catalytic reaction systems will be the subject of a forthcoming paper [9].

Method B, when applied to cyclopentadienyliron carbonyl derivatives, leads to binuclear reaction products: When $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$ or $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ is treated with equivalent amounts of $\text{Fe}_2(\text{CO})_9$ in refluxing THF, and then freed from unreacted $\text{Fe}_2(\text{CO})_9$, iron-containing compounds are formed to which we assign, from their mass spectral and IR spectral data, the binuclear compositions $[(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ and $[(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$. The IR data of these materials are virtually identical to those of the known compound $[(\text{CH}_3)_3\text{SiC}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ [10]. Treatment of silica gel supports with these dimeric ethoxysilylcyclopentadienyliron dicarbonyl compounds leads, as expected, to the formation of surface-bound binuclear iron carbonyl species. The IR spectra of these materials show the same absorptions, in particular that of a bridging CO group at 1790 cm^{-1} , as the corresponding homogeneously dissolved binuclear cyclopentadienyliron carbonyl compounds. Interestingly, a significant broadening of this $\mu\text{-CO}$ absorption at 1790 cm^{-1} and a change in the relative intensities of the two bands at 1960 and 2000 cm^{-1} is observable in the IR spectra of these SiO_2 -supported compounds. We interpret these effects as an indication that the steric constraints of surface linkages distort at least part of these binuclear species from their equilibrium geometries [11].

To gain additional insight into the mode of bonding of these binuclear species to the SiO_2 surface, we have further performed some additional chemical reactions of the materials. Cleavage of the binuclear iron carbonyl derivatives is brought about by treatment with iodine in CHCl_3 ; the products of this cleavage reaction can be assumed, on the basis of their $\nu(\text{CO})$ IR absorptions, which are identical to those of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ [12], and of an elemental composition with a Fe/I ratio close to 1.0, to be SiO_2 -linked derivatives of the corresponding silylcyclopentadienyl iododiron dicarbonyl. About 15–20% of the original iron content of the binuclear, SiO_2 -bound compounds is transferred into solution by this cleavage as a soluble silylcyclopentadienylidodiron dicarbonyl, possibly in form of dimeric species containing Si—O—Si bridges; the main part (80–85%) of the original iron content remains linked to the SiO_2 support. Conversion of these iodo dicarbonyl derivatives into the corresponding hydrido dicarbonyl species was effected by treatment with lithium borohydride in THF solution [13], as judged from a shift in the $\nu(\text{CO})$ absorptions by about $30\text{--}35 \text{ cm}^{-1}$ to values similar to those observed in the SiO_2 -supported silylcyclopentadienyliron dicarbonyl hydride, obtained by Method A, as described before. As with the corresponding materials obtained by Method A, the iron dicarbonyl species obtained from the binuclear surface compound via the iodo dicarbonyl derivative and subsequent reaction with LiBH_4 show only very minor $\mu\text{-CO}$ absorptions below 1800 cm^{-1} , even after heating to $150\text{--}180^\circ\text{C}$. This observation



SCHEME 1. Reaction paths of SiO₂-bound dimethylsilylcyclopentadienyl-iron and -cobalt carbonyl derivatives. Similar reaction patterns pertain for the corresponding species derived from triethoxysilylcyclopentadienyl compounds.

indicates that most of the iron centers of the binuclear surface compound are permanently separated from each other once the Fe—Fe bond is cleaved, possibly by release of strain in those species which are attached to the SiO₂ surface through both silylcyclopentadienyl anchoring groups; alternatively, if the binuclear units had been linked to the SiO₂ surface only through one of their two moieties, the liberated subunit would migrate to an independent surface site*.

An essentially identical reaction product is obtained more directly when the SiO₂-bound silylcyclopentadienyliron dicarbonyl dimer is exposed to an elevated pressure of H₂ (about 100 atm) in benzene solution at 120°C for 4 h. A small residual absorption intensity at 1790 cm⁻¹ indicates that all but a minor fraction (ca. 10–20%) of the Fe—Fe-bonded binuclear species are permanently converted under these conditions into mononuclear silylcyclopentadienylhydridoiron dicarbonyl units. This observation demonstrates that it is in principle feasible to introduce cyclopentadienylmetal carbonyl compounds onto the surface of SiO₂ supports in form of air-stable binuclear species. Cleavage of these surface-bound dimers, e.g. under catalytic reaction conditions, would then lead to rearrangement of the surface linkages so as to stabilize more reactive, mononuclear cyclopentadienylmetal carbonyl species.

The various reaction paths established for SiO₂-bound cyclopentadienyl-iron and -cobalt carbonyl derivatives are summarized in Scheme 1.

Experimental

All operations described below, were unless specified otherwise, carried out under dinitrogen in Schlenk vessels or on a high-vacuum manifold. Metal contents were determined spectrophotometrically with nitroso-R-salt for Co and with 1,10-phenanthroline for Fe after degradation of the SiO₂ support materials with 40% aqueous HF. Carbon—hydrogen analyses were performed by the Analytical Laboratory, Universität Stuttgart. The support material used for the syntheses described below is a silica gel, purchased from Ventron Co (Stock Nr. 89346), for which a pore volume of 1 ml/g, a specific surface of 300 m²/g and a granular size of 8–12 mesh are specified. This silica gel was dried at temperatures up to 800°C for several hours and outgassed overnight at 80–100°C in vacuo.

1. Preparation of SiO₂-supported silylcyclopentadienyl-iron and -cobalt derivatives (Method A)

Synthesis of (C₂H₅O)Si(CH₃)₂C₅H₅ and (C₂H₅O)₃SiC₅H₅ was carried out as described in the literature [4,14]. For the attachment of these silanes to the silica gel surface, 15 g silica gel were suspended in toluene and pretreated, at 60–80°C with 0.1 ml of a 0.1 M aqueous NaOH solution. To this suspension were then added 5 ml (ca. 30 mmol) of the relevant silane, and the mixture was kept at 60–80°C for 2 days. The silica gel was then isolated and washed with toluene. Subsequent washings with chloroform, acetone, and methanol

* The elemental composition of these materials, noted above, indicates that only about 75% of the reactive Si—OH sites are occupied in the silica gel containing the silylcyclopentadienyliron dicarbonyl dimer, so that a measurable binding capacity is still available for the cleaved-off subunits.

were performed without exclusion of air. The functionalized silica gel was finally dried overnight at 80–100°C in vacuo.

For the introduction of iron carbonyl groups, a 15 g sample of the silylcyclopentadiene-functionalized silica gel was refluxed for 2 days with 20 mmol of $\text{Fe}_2(\text{CO})_9$ in THF. The silica gel, which was now red-brown, was isolated, washed with air-free THF until the eluents were colourless, and dried at 80–100°C in vacuo.

The reaction of $\text{Co}_2(\text{CO})_8$ was carried out analogously, but with CH_2Cl_2 instead of THF as solvent. The properties of the materials so obtained are described in the Results and discussion section.

2. Preparation and reactions of $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4\text{Co}(\text{CO})_2$ and $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_4\text{Co}(\text{CO})_2$ (Method B)

$\text{Co}_2(\text{CO})_8$ (6.2 g, 18 mmol) was treated with 7 ml (43 mmol) of $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ in refluxing CH_2Cl_2 for 12 h. The mixture was filtered and the filtrate evaporated in vacuo. The residual red oil was cooled to -78°C and separated from some unchanged solid $\text{Co}_2(\text{CO})_8$ by means of a syringe. The resulting compound was characterized by its mass spectrum with a parent ion at m/e 342 for $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_4\text{Co}(\text{CO})_2$ and appropriate fragment ions. Its IR spectrum shows two $\nu(\text{CO})$ absorptions at 2020 and 1965 cm^{-1} , with only minimal absorptions around 1865 cm^{-1} , indicating the absence of any significant amounts of $\text{Co}_2(\text{CO})_8$. Reactions of $\text{Co}_2(\text{CO})_8$ with $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$ was carried out analogously to yield a corresponding cobalt dicarbonyl derivative with closely similar spectral properties.

Heating 4 ml of each of these silylcyclopentadienylcobalt dicarbonyl compounds with 6 g of silica gel in toluene at 80°C for 12 h, and subsequent washing with toluene gave a surface compound with the SiO_2 support material which had spectral properties very similar to those of the corresponding material obtained by Method A.

3. Preparation and reactions of $[(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ and $[(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$

A mixture of 3.35 g (0.2 mmol) of $\text{Fe}_2(\text{CO})_9$ and 1.8 ml (ca. 8 mmol) of $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_5$ in 50 ml THF was heated to reflux for 4 h. The dark red solution was filtered and the THF evaporated. The red oil was taken up in petroleum ether and separated from an insoluble residue of $\text{Fe}_2(\text{CO})_9$. Removal of solvent yielded $[(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ as a dark red wax. This product was characterized by a mass spectrum with a parent ion at m/e 680 and the fragment ions expected for such a compound. In its IR spectrum $\nu(\text{CO})$ bands are observed at 2050, 2000, 1960 and 1795 cm^{-1} . The NMR spectrum contains two signals at τ 4.20 and 4.85 ppm, these data are in close agreement with those reported for the related compound $[(\text{CH}_3)_3\text{SiC}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ [10].

The reaction of $(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_5$ with $\text{Fe}_2(\text{CO})_9$ was carried out analogously to yield the corresponding compound $[(\text{C}_2\text{H}_5\text{O})\text{Si}(\text{CH}_3)_2\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$.

A sample (8–10 mmol) of each of these silylcyclopentadienyliron dicarbonyl dimers was then heated to 80–100°C with about 15 g of silica gel in toluene suspension for about 8 h. The silica gel was isolated, transferred to a Soxhlet

extractor, extracted with diethyl ether until the eluents were colourless, and finally dried at 80°C in vacuo. The physical and chemical properties of the resulting material are described in the Results and discussion section.

Acknowledgements

We wish to thank The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work, and the Donegani Research Institute for a leave of absence for Dr. Gubitosa.

References

- 1 (a) G. Gubitosa, M. Boldt and H.H. Brintzinger, *J. Amer. Chem. Soc.*, **99** (1977) 5174; (b) G. Gubitosa and H.H. Brintzinger, *J. Organometal. Chem.*, **140** (1977) 187.
- 2 J.C. Bailar, Jr., *Catal. Rev. Sci. Eng.*, **10** (1974) 17; R. Grubbs, C.P. Lau, R. Cukier and C. Brubaker, Jr., *J. Amer. Chem. Soc.*, **99** (1977) 4517.
- 3 H.H. Wheelall, *Science*, **166** (1969) 615; K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C. Pitkethly and P.J. Robinson, *J. Organometal. Chem.*, **87** (1975) 203; **107** (1976) 393.
- 4 R. Jackson, J. Ruddlesden, D.J. Thompson and R. Whelan, *J. Organometal. Chem.*, **125** (1977) 57.
- 5 V.L. Snoeyink and W.J. Weber, Jr., in D.F. Danielli, M.D. Rosenberg and D.A. Cadenhead (eds.), *Progress in Surface and Membrane Science*, Academic Press, New York, London, 1972, Vol. 5, p. 63.
- 6 T.S. Piper, F.A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1** (1955) 165.
- 7 R.B. King, *Z. Naturforsch. B*, **19** (1964) 1160.
- 8 A. Davison, J.A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1963) 1133.
- 9 G. Gubitosa and H.H. Brintzinger, in preparation.
- 10 E.W. Abel and S. Moorhouse, *J. Organometal. Chem.*, **28** (1971) 211; **29** (1971) 227.
- 11 R.D. Fischer, A. Vogler and K. Noack, *J. Organometal. Chem.*, **7** (1967) 135; F.A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6** (1967) 15.
- 12 T.S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2** (1956) 38.
- 13 M.L.H. Green, C.N. Street and G. Wilkinson, *Z. Naturforsch. B*, **14** (1959) 738.
- 14 K.C. Frisch, *J. Amer. Chem. Soc.*, **75** (1953) 6050.
- 15 W. Hertl, *J. Phys. Chem.*, **72** (1968) 1248, 3993.