Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

FERROCENYL- AND (PENTACHLOROPHENYL)CARBENE COMPLEXES OF CHROMIUM*

G. A. MOSER**, E. O. FISCHER AND M. D. RAUSCH**
Anorganisch-chemisches Laboratorium der Technischen Universität München (Deutschland)

(Received November 12th, 1970)

SUMMARY

The reactions of pentachlorophenyllithium as well as ferrocenyllithium with chromium hexacarbonyl, followed by treatment with trialkyloxonium tetrafluoroborate salts, lead to alkoxy(pentachlorophenyl)- and alkoxyferrocenyl-carbene–pentacarbonyl-chromium complexes. Studies on the carbonyl stretching frequencies in these complexes are in agreement with the known electron-withdrawing and electron-releasing nature of pentachlorophenyl and ferrocenyl groups, respectively.

INTRODUCTION

After the first report[1] in 1964 concerning the existence of a tungsten carbonyl carbene complex, much work has been done in an attempt to elucidate the structure, bonding and reactivity of many Group VI carbene complexes. Initially, these carbene complexes were prepared by treating the appropriate metal hexacarbonyl with an organolithium reagent, followed by acid hydrolysis to yield a rather unstable hydroxy complex. The final step of the reaction involved the insertion of CH_2 derived from CH_2N_2 into the O–H bond to give $(CO)_5M{-}C(OCH_3)R$. This procedure subsequently was improved by using $[(CH_3)_3O](BF_4)$ as a methylating agent for the organolithium adduct[2].

As part of our overall program concerning the structure and bonding of stable transition metal carbonyl carbene complexes, we felt it would be of interest to investigate the properties of carbene complexes containing both ferrocenyl and pentachlorophenyl substituents. It is well-known that σ-bonded pentachlorophenyl derivatives of transition metals exhibit remarkably enhanced stabilities[3,4], and since ferrocene itself is quite stable, the preparation of carbene complexes derived from ferrocenyl- and (pentachlorophenyl)lithium reagents was attempted.

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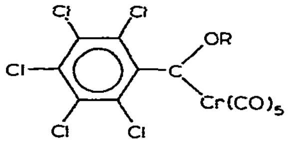
* Presented at the 13th International Conference on Coordination Chemistry, Zakopane, Poland, September 19th, 1970.

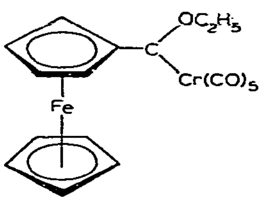
** Present address: Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002 (U.S.A.)

RESULTS AND DISCUSSION

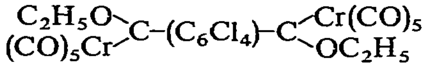
(Pentachlorophenyl)carbene complexes (I) and (II) were prepared by the reaction of (pentachlorophenyl)lithium and chromium hexacarbonyl in ethyl ether at −78°, followed by treatment with the appropriate trialkyloxonium tetrafluoroborate salt. A small amount of an additional orange crystalline compound was obtained during the chromatographic purification of (I). Mass spectroscopic and elemental analysis data support a structure as follows:



(I) R = C_2H_5
(II) R = CH_3



(III)



$$\begin{matrix} C_2H_5O \\ (CO)_5Cr \end{matrix}\!\!>\!C\text{-}(C_6Cl_4)\text{-}C\!<\!\!\begin{matrix} Cr(CO)_5 \\ OC_2H_5 \end{matrix}$$

Undoubtedly, this compound results from the presence of a small amount of the dilithio reagent $C_6Cl_4Li_2$ which is formed during the preparation of (pentachlorophenyl)lithium. The preparation of the ferrocenylcarbene complex (III) also proceeded in good yield when ferrocenyllithium was allowed to react with chromium hexacarbonyl at −78°. Addition of triethyloxonium tetrafluoroborate led to the formation of (III)*.

The NMR spectra of (I) and (III) support the proposed structures. The spectrum of (III) in C_6D_6 at 35° exhibits a characteristic singlet at τ 5.79 for the unsubstituted cyclopentadienyl ring protons, and a typical[6] A_2B_2 pattern (apparent triplets at τ 5.25 and τ 5.02) for the substituted cyclopentadienyl ring protons. The quartet representing the methylene protons at τ 4.96 overlaps the A_2B_2 resonance at 60 MHz, however, good resolution was obtained at 100 MHz. The methyl protons appear as a triplet ($J = 12$ Hz) at τ 8.38. Complex (I) exhibits a temperature dependent NMR spectrum. The expected quartet due to the methylene group of (I) was not observed in acetone-d_6 at 35°, however, upon cooling the sample to −10°, the quartet (τ 5.44) became well-defined. On the other hand, the upfield triplet at τ 8.38 representing the methyl protons remained sharp throughout the temperature range investigated (−20° to +40°). Further studies to elucidate the nature of this process, which may be due to restricted rotation around the carbene carbon, are currently in progress.

Evidence for the electronic nature of the aryl group bonded to the carbene carbon in these new complexes was obtained by comparing the ν(CO) stretching frequencies of a series of complexes (Table 1).

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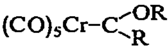
* After completion of this work (May, 1970), an independent study concerning the NMR spectra of several ferrocenylcarbene complexes was briefly described[5].

TABLE I

ν(CO) STRETCHING FREQUENCIES OF SOME CARBENE–CHROMIUM COMPLEXES,



$(CO)_5Cr{-}C{<}^{OR'}_{R}$ [a]

Complex	R'	R	A_1	A_1	E	B_1	Ref.
(V)	CH_3	C_6H_5	2060	1963	1952	1986	7
(IV)	CH_3	p-$(CH_3)_2NC_6H_4$	2054	1943	1935	1976	7
(III)	C_2H_5	$C_{10}H_9Fe$	2055	1947	1934	1976	[b]
(I)	C_2H_5	C_6Cl_5	2070	1972	1955	1998	[b]
(II)	CH_3	C_6Cl_5	2070	1973	1955	1996	[b]
(VI)	CH_3	p-ClC_6H_4	2063	1964	1952	1986	7

[a] Measured in n-hexane and given in cm^{-1}. [b] This work.

The lower ν(CO) stretching frequencies in (IV) compared to (V) are attributable to a transfer of electron density onto the carbene carbon and further onto the $Cr(CO)_5$ group. A similar result is found for (III), in agreement with the known strongly electron-releasing nature of the ferrocenyl group. On the other hand, the ν(CO) frequencies for (I) and (II) are raised compared to (V) and even (VI). This finding is in accord with the highly electronegative nature of the pentachlorophenyl group. In the case of (I) and (II), the nature of the R' group does not appear to affect the ν(CO) stretching frequencies to any significant extent.

EXPERIMENTAL

Preparation of ethoxyferrocenylcarbene–pentacarbonylchromium (III)

Ferrocenyllithium was prepared from bromoferrocene (1.00 g, 3.78 mmole) and n-butyllithium in hexane (2.34 ml, 3.78 mmole) in dry N_2-saturated ethyl ether solution[8]. The solution was cooled to −78°. Chromium hexacarbonyl (0.831 g, 3.78 mmole) in 250 ml of dry ether was cooled to −78° and the orange solution of ferrocenyllithium was added to the chromium hexacarbonyl solution in one portion. The resulting mixture was allowed to warm to room temperature at its own rate while it was rapidly stirred. After 3 h of stirring, the ether was removed under reduced pressure yielding an orange solid. Nitrogen-saturated water (150 ml) was added to this solid yielding an orange colored solution. Triethyloxonium tetrafluoborate (0.719 g, 3.78 mmole) was added in one portion and the solution turned purple. Hexane (100 ml) was added and stirring was continued for 15 min. After this time, the hexane was separated from the aqueous layer, the latter was successively extracted with hexane (2 × 100 ml) and ethyl ether (2 × 100 ml), and the organic layers were combined. Evaporation of the solvent yielded dark purple crystals. Recrystallization from pentane gave 1.30 g of deep purple crystalline (III), m.p. 129° (sealed tube under N_2). The yield was 79%. [Found: C, 49.92; H, 3.36; Fe, 12.96; O, 22.5; mol.wt. (*m/e*), 434. $C_{18}H_{14}CrFeO_6$ calcd.: C, 49.79; H, 3.26; Fe, 12.86; O, 22.11%; mol.wt., 434.]

Preparation of alkoxy(pentachlorophenyl)carbene–pentacarbonylchromium complexes (I) and (II)

(Pentachlorophenyl)lithium was prepared from hexachlorobenzene (2.00 g, 7.03 mmole) and n-butyllithium in hexane (4.41 ml, 7.03 mmole) in ethyl ether at $-78°$[9]. Following the above procedure, the lithium reagent was allowed to react with chromium hexacarbonyl (1.55 g, 7.03 mmole) and then triethyloxonium tetrafluoborate (1.34 g, 7.03 mmole) was added. The crude product was chromatographed on silica gel under nitrogen (40 × 1.5 cm, hexane elution) and produced two colored bands. Evaporation of the first band gave yellow-orange crystals of (I) in 21% yield, m.p. 104° (sealed tube under N_2) [Found: C, 34.16; H, 1.06; Cr, 10.64; mol.wt. (*m/e*), 498. $C_{14}H_5Cl_5CrO_6$ calcd.: C, 33.73; H, 1.02; Cr, 10.43 %; mol.wt., 498.]

Evaporation of the second band gave a small amount of an orange compound, m.p. 123° (sealed tube under N_2) [Found: C, 37.50; H, 1.60; Cl, 19.92; mol.wt. (*m/e*), 712. $C_{22}H_{10}Cl_4Cr_2O_{12}$ calcd.: C, 37.10; H, 1.42; Cl, 19.92 %; mol.wt., 712.]

Complex (II) was prepared in a similar manner with the exception that trimethyloxonium tetrafluoroborate (1.04 g, 7.03 mmole) was used. Complex (II) was isolated as orange crystals, m.p. 116.5° (sealed tube under N_2) in 28% yield. (Found: C, 32.68; H, 0.72; Cr, 10.85. $C_{13}H_3Cl_5CrO_6$ calcd.: C, 32.23; H, 0.62; Cr, 10.74%.)

ACKNOWLEDGEMENTS

The authors are very grateful to the National Science Foundation for partial support of this research program. One of us (M.D.R.) is also deeply indebted to the Alexander von Humboldt-Stiftung for a research fellowship during the period Sept., 1969, to June, 1970.

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