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Organometallic Complexes Derived by Reaction of Transition Metal–2-Alkenyl and –2-Alkynyl Compounds with Hexafluoroacetone[1]

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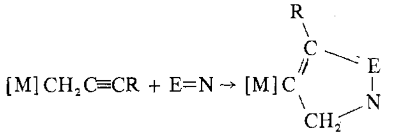
A series of transition metal–vinyl derivatives containing a substituted dihydrofuranato ring, $[M]\overline{C{=}C(R)C(CF_3)_2OC}H_2$ (I), and of transition metal–alkyl derivatives containing a substituted tetrahydrofuranato ring, $[M]\overline{C(R)C(R')(R'')C(CF_3)_2OC}H_2$ (II), were prepared by reaction of the appropriate 2-alkynyl and 2-alkenyl complexes, respectively, with hexafluoroacetone. The new compounds include I, where $[M] = Mn(CO)_5$ and η^5-$C_5H_5Fe(CO)_2$, R = CH_3 and C_6H_5; $[M] = \eta^5$-$C_5H_5Mo(CO)_3$, R = C_6H_5; and II, where $[M] = Mn(CO)_5$ and η^5-$C_5H_5Mo(CO)_3$, R = R' = H, R'' = C_6H_5; $[M] = \eta^5$-$C_5H_5Fe(CO)_2$, R = H, R' = R'' = CH_3 and R = R' = H, R'' = H, CH_3, C_6H_5, and Cl; $[M] = \eta^5$-$C_5H_5W(CO)_3$, R = R' = H, R'' = H and CH_3. A similar reaction of η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ with hexafluoroacetone afforded the expected cycloadduct II, η^5-$C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OC}H_2$, as well as η^5-$C_5H_5Fe(CO)_2OC(CF_3)_2CH_2C({=}CH_2)CH_2C(CF_3)_2OH$. Complexes of type II with $[M] = \eta^5$-$C_5H_5Fe(CO)_2$, R = H, and R' ≠ R'' show four infrared ν_{CO} bands in pentane; possible explanations for this phenomenon are considered. Photolysis in the presence of triphenylphosphine of some complexes I and II containing $[M] = \eta^5$-$C_5H_5Fe(CO)_2$ yields the corresponding substituted monocarbonyls. The aforementioned reactions with hexafluoroacetone are compared with other related (3 + 2) cycloaddition reactions involving transition metal–carbon σ-bonded complexes. The infrared ν_{CO} absorptions of a number of products of the type η^5-$C_5H_5Fe(CO)_2\overline{C{=}C(C_6H_5)ENC}H_2$ (E=N = electrophilic molecule) have been tabulated for comparison.

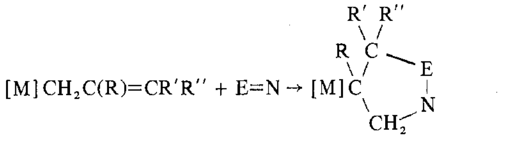
Introduction

The addition of electrophilic reagents of the type E=N (E = electrophilic part, N = nucleophilic part) to transition metal–2-alkenyl and –2-alkynyl complexes has afforded a number of organometallic products.[2,3] With the 2-alkynyls, (3 + 2) cycloaddition accompanied by 1,2 metal migration invariably occurs to yield vinylic species containing a five-membered ring (eq 1). However, with the 2-alkenyls, either


(1)

e.g., $[M] = \eta^5$-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$, $Mn(CO)_5$; R = CH_3, C_6H_5; E=N = SO_2,[4] SO_3,[5] $(CN)_2C{=}C(CN)_2$,[6] $ClSO_2NCO$,[7] $CH_3OC(O)NSO_2$[8]

analogous cycloaddition (eq 2) or insertion (eq 3) has been


(2)

e.g., $[M] = \eta^5$-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$; R, R', R'' = H, CH_3, C_6H_5; E=N = $(CN)_2C{=}C(CN)_2$,[6,9] $ClSO_2NCO$,[7] $CH_3OC(O)NSO_2$[2]

$$[M]CH_2C(R){=}CR'R'' + E{=}N \rightarrow [M]N{-}E{-}CH_2C(R){=}CR'R'' \text{ and/or } [M]N{-}E{-}C(R')(R'')C(R){=}CH_2 \quad (3)$$

e.g., $[M] = \eta^5$-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_2P(OC_6H_5)_3$, $Mn(CO)_5$; R, R', R'' = H, CH_3, C_6H_5; E=N = SO_2,[3,10] $(CN)_2C{=}C(CN)_2$,[6] $ClSO_2NCO$,[7a] $SnCl_2$[11]

reported.

As part of a continuing investigation of these reactions we studied the behavior of the electrophile hexafluoroacetone. Electrophilic reactions of hexafluoroacetone with transition metal complexes are well documented. For example, this ligand is known to undergo oxidative addition to nickel(0), palladium(0), and platinum(0) complexes to yield products with metal-containing three- and five-membered rings.[12] Cycloaddition of hexafluoroacetone to the η^4-cycloheptatriene and η^4-cyclooctatetraene rings in the respective iron tricarbonyl complexes has also been reported.[13] With various η^4-1,3-diene complexes of iron and rhodium, hexafluoroacetone undergoes mono- or diinsertion reactions into metal–carbon bonds.[14]

We here report in detail the results of our study on the addition of hexafluoroacetone to transition metal–2-alkenyl and –2-alkynyl complexes.

Experimental Section

Materials. Hexafluoroacetone gas (bp −27°) was obtained from Columbia Organics and was used as received. Tetrahydrofuran (THF) and pentane were distilled under nitrogen from $LiAlH_4$ and CaH_2, respectively, prior to use. Other chemicals and solvents procured commercially were reagent grade and were used without further purification.

η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ (R = CH_3[4a] and C_6H_5[15]), η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$,[4c] $Mn(CO)_5CH_2C{\equiv}CR$ (R = CH_3[4a] and C_6H_5[4c]), η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ (R = R' = H, R'' = H,[16] CH_3,[16] C_6H_5,[17] and Cl;[17] R = H, R' = R'' = CH_3;[17] R = CH_3, R' = R'' = H[6]), η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$,[17] and $Mn(CO)_5CH_2CH{=}CHC_6H_5$[18] were prepared by the specified literature methods. Samples of η^5-$C_5H_5W(CO)_3CH_2CH{=}CHR$ (R = H and CH_3) were supplied by Dr. S. R. Su.

Analyses and Physical Measurements. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Hydrogen-1 NMR spectra were recorded with a Varian Associates A-60A spectrometer using tetramethylsilane as reference. Fluorine-19 NMR spectra were obtained by Dr. J. L. Peterson and Mr. J. M. Geckle with a Varian Associates HA-100 spectrometer at 94.1 MHz using $C_6H_5CF_3$ as the solvent and lock. All tabulated infrared ν_{CO} values were obtained using a Beckman IR-9 spectrophotometer; routine infrared spectra were recorded with a Perkin-Elmer Model

337 spectrophotometer. Mass spectra were obtained by Mr. C. R. Weisenberger with an AEI Model MS-9 spectrometer.

Preparation of Metal–Etherato Cycloaddition Complexes. Method A. In Neat Hexafluoroacetone. In a typical reaction, $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.35 g, 1.2 mmol) in ca. 6 ml of liquid hexafluoroacetone was stirred for 9 hr in a nitrogen atmosphere under a Dry Ice condenser, with the hexafluoroacetone refluxing continuously. The excess hexafluoroacetone was then allowed to evaporate and the resultant orange solid was dissolved in a minimum of chloroform. This solution was eluted with chloroform over a 2.5 × 25 cm column of Florisil to produce a broad yellow band. The band was collected and the effluent was concentrated to yield an orange-yellow solid. After washing with three 30-ml portions of pentane, 0.18 g (33% yield) of yellow microcrystals of the product was obtained.

Details of the synthesis as well as analytical data and physical properties of this and all other new metal–etherato cycloaddition complexes prepared herein are provided in Table I.

When a similar reaction was run for ca. 15 min, only a 5% yield of the cycloaddition product was obtained. The remainder of the starting metal–2-alkynyl complex was recovered unreacted.

Attempts at reaction between hexafluoroacetone and various transition metal–2-alkenyl complexes in refluxing neat hexafluoroacetone were unsuccessful. In each case the 2-alkenyl complex was recovered in quantitative yield.

Method B. In Organic Solvents. (a) General Preparation. An excess of hexafluoroacetone (ca. 1 ml of liquid) was condensed onto $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$ (1.15 g, 3.92 mmol) in 10 ml of CH_2Cl_2 and the resulting solution was stirred for 30 min under a Dry Ice condenser in a nitrogen atmosphere. Concentration at 25° (ca. 20 Torr) afforded a red oil which was dissolved in 150 ml of 1:5 (v/v) CH_2Cl_2–pentane. The resulting solution was filtered through 3 cm of alumina (10% H_2O) and the filtrate was evaporated to an orange solid. Washing with two 25-ml portions of pentane and air-drying left yellow crystals, 1.43 g (79% yield). Concentration of the washes yielded 0.08 g more of slightly darker, yellow microcrystals.

A similar reaction in benzene for ca. 1 hr afforded the cycloaddition product in 77% yield.

(b) $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$. Excess hexafluoroacetone was condensed onto a solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ (2.21 g, 9.55 mmol) in 10 ml of CH_2Cl_2 under nitrogen. The initial reaction appeared to be exothermic, in contrast to the other addition reactions of hexafluoroacetone in which no significant heating was observed. The hexafluoroacetone was allowed to reflux under a Dry Ice condenser for 30 min and volatile materials were then evaporated in vacuo to leave a dark red, viscous oil, 4.36 g. This yield corresponds to approximately 1.3 molecules of hexafluoroacetone for every molecule of the 2-alkenyl complex employed.

The oil was dissolved in a minimum of 1:1 (v/v) CH_2Cl_2–pentane and this solution was filtered through 3 cm of alumina (6% H_2O). The alumina was washed with more 1:1 (v/v) CH_2Cl_2–pentane and the filtrate was concentrated to a red oil. Washing the oil rapidly with pentane left a mustard-colored solid, 0.75 g (20% yield), identified as $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OC}H_2$. This solid was readily purified by recrystallization from 1:4 (v/v) CH_2Cl_2–pentane or by column chromatography on alumina to give golden yellow crystals.

The pentane washes from the above work-up were concentrated to yield a dark red solid, 1.09 g. This material was composed of a small amount of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OC}H_2$ and another, red product. The latter product could be obtained pure with difficulty by crystallization from pentane to afford red crystals, 0.84 g (16% yield), mp ca. 95° dec. The crystals analyze for $\eta^5\text{-}C_5H_5Fe(CO)_2C_4H_7{\cdot}2(CF_3)_2CO$. Anal. Calcd for $C_{17}H_{12}F_{12}FeO_4$: C, 36.20; H, 2.14. Found: C, 36.46; H, 2.27. Ir spectrum (pentane, ν_{CO} region, cm^{-1}): 2065 vs, 2023 vs. ^1H NMR spectrum ($CDCl_3$, τ): 7.5–6.8 (m, 4 H, $-CH_2-$), 5.55–5.1 (m, 3 H, $=CH_2$ and $-OH$), 4.91 (s, 5 H, C_5H_5). ^{19}F NMR spectrum ($C_6H_5CF_3$, ϕ): 72.2 (s, 6 F), 77.2 (s, 6 F).

Thermal Decomposition of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OC}H_2$. A sample of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OC}H_2$ was heated at 90° under nitrogen for 24 hr. Red needles of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ sublimed in low yield (<10%). No other carbonyl-containing product was noted.

Thermal Decomposition of $\eta^5\text{-}C_5H_5Fe(CO)_2C_4H_7{\cdot}2(CF_3)_2CO$. The title compound, 0.84 g, was heated under nitrogen (760 Torr) for 3 hr at 105–115°. White needles, 0.18 g, were collected by sublimation. The residue showed no carbonyl-containing species other than a very small amount of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

The white solid may be resublimed readily at 65° (760 Torr) or 25° (0.1 Torr) to form larger needles, mp 146–147.5° (lit.[19b] mp 149–150°). The same white product is noted when the title compound decomposes in solution for several hours or in the solid for several days at room temperature. Ir spectrum (KBr pellet, cm^{-1}): 3360 s, 2960 vw, 2935 w, 2860 w, 2480 m, 1640 w, 1635 m, 1276 vs, 1226 vs, 1155 s, 1135 s, 1031 s, 1017 s, 983 m, 952 m, 928 m, 875 w, 829 w, 771 w, 731 m, 706 m, 688 s. ^1H NMR spectrum ($CDCl_3$ τ): 7.01 (s, 4 H), 5.54 (s, br, 2 H), 4.69 (s, 2 H). ^{19}F NMR spectrum ($C_6H_5CF_3$, ϕ): 77.6 (s). The mass spectrum (70 eV, source temperature 60°) shows a parent ion peak at *m/e* 388, as well as strong peaks due to the loss of H_2O and CF_3 groups from the parent ion. All these data implicate the solid as the known[19] $H_2C{=}C[CH_2C(CF_3)_2OH]_2$.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{CHCH_2C(CF_3)_2OC}H_2$. A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH_2C(CF_3)_2OC}H_2$ (0.19 g, 0.49 mmol) and triphenylphosphine (0.19 g, 0.72 mmol) in 30 ml of THF was photolyzed at 350 nm in a Rayonet Model RPR-100 reactor (all 16 lamps) for 4 hr under nitrogen. Evaporation to dryness gave a red-orange solid which was then dissolved in 10 ml of 1:4 (v/v) CH_2Cl_2–pentane. This solution was chromatographed on a 2.5 × 12 cm column of alumina (6% H_2O). Elution with 1:1 (v/v) CH_2Cl_2–pentane rapidly moved an orange band which was collected as a deep orange solution and concentrated to an oil. The oil was then dissolved in 50 ml of pentane. Slow cooling and concentration to ca. 1 ml afforded bright red crystals, 0.07 g (22% yield). Once obtained in a pure state this compound is not appreciably soluble in pentane; it is soluble in more polar solvents such as benzene, dichloromethane, and chloroform.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{CHCH(C_6H_5)C(CF_3)_2OC}H_2$. A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH(C_6H_5)C(CF_3)_2OC}H_2$ (0.35 g, 0.76 mmol) and $P(C_6H_5)_3$ (0.21 g, 0.80 mmol) in 45 ml of THF was photolyzed for 2 hr as described above. The resultant red solution was concentrated (ca. 20 Torr) to a viscous oil. The oil was dissolved in a minimum of 1:1 (v/v) benzene–pentane and this solution was eluted over a 2.5 × 8 cm Florisil column with the same solvent mixture. A single bright orange band was collected and concentrated to a red oil. The oil was dissolved in 15 ml of pentane and the resulting solution was slowly concentrated at 25° (ca. 20 Torr) to yield an orange solid, 0.21 g (40%). The pure complex is insoluble in pentane but soluble in benzene and chloroform.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{C{=}C(C_6H_5)C(CF_3)_2OC}H_2$. Triphenylphosphine (0.16 g, 0.61 mmol) and $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C{=}C(C_6H_5)C(CF_3)_2OC}H_2$ (0.25 g, 0.55 mmol) in 40 ml of THF were irradiated for 2 hr under helium. Evaporation of the solvent gave a red oil which foamed to a red glass. This material was dissolved in a minimum of benzene and the resulting solution was eluted with benzene over a 2.5 × 6 cm column of Florisil. A single red band was collected and the effluent was concentrated to a red oil. Redissolving in benzene, diluting with hexane, and slowly concentrating at 25° (ca. 20 Torr) yielded red crystals, which were washed with pentane; yield 0.18 g (47%).

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH(CH_3)C(CF_3)_2OC}H_2$ with HCl. Hydrogen chloride was bubbled through a solution of the title complex (0.15 g) in 25 ml of pentane at room temperature for 30 min. The yellow solution became cloudy almost immediately and a red oil formed. Evaporation of the pentane at 25° (ca. 20 Torr) gave a red-orange solid. Ir spectroscopy indicated this solid to be ca. 40% starting carbonyl complex and ca. 60% $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH_2C(CF_3)_2OC}H_2$ with HCl. Hydrogen chloride was bubbled through a solution of the title complex (0.08 g) in 10 ml of benzene for 4 hr at room temperature. The solvent was then evaporated to leave a red-orange solid, ca. 0.06 g, shown to be 90% $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$ and 10% unreacted carbonyl complex by ir spectroscopy.

Attempted Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH_2C(CF_3)_2OC}H_2$ with SO_2. A solution of the title complex (0.10 g) in 3 ml of liquid SO_2 was kept a reflux for 3 hr under a Dry Ice condenser. The SO_2 was then allowed to evaporate to give a sticky orange solid. Recrystallization of this solid from pentane afforded the unreacted carbonyl complex as yellow crystals, 0.08 g. No SO_2 insertion product was observed.

Attempted Reaction of $\eta^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{C{=}C(C_6H_5)}$-

Table I. Details of the Synthesis, Analytical Data, and Physical Properties of Complexes of the type $[M]\overline{C{=}C(R)C(CF_3)_2OCH_2}$ (I) and $[M]\overline{C(R)C(R')(R'')C(CF_3)_2OCH_2}$ (II)

Complex				Prepn					Analyses, %				Mol wt	
									C		H			
[M]	R	R'	R''	Method[a]	Time, hr	Yield, %	Mp, °C	Color	Calcd	Found	Calcd	Found	Calcd[b]	Found[c]
	I													
$Mn(CO)_5$	CH_3			A	0.25	66	107–107.5	White	34.81	34.69	1.22	1.19	414	414
$Mn(CO)_5$	C_6H_5			A	3	63	112–113	White	42.88	42.96	1.48	1.48	476	476
$\eta^5\text{-}C_5H_5Fe(CO)_2$	CH_3			A	0.75	55	140.5–141.5	Golden yellow	42.46	42.57	2.55	2.41	396	396
$\eta^5\text{-}C_5H_5Fe(CO)_2$	C_6H_5			B (A)	0.5 (9)	88 (33)	148–149	Yellow	49.81	49.79	2.64	2.65	458	458
$\eta^5\text{-}C_5H_5Mo(CO)_3$	C_6H_5			B (A)	0.5 (0.3)	57 (18)	150–151 dec	Yellow	45.65	45.68	2.30	2.41	528	528
$\eta^5\text{-}C_5H_5Fe(CO)L$[d]	C_6H_5			C	2	47	193 dec	Red	62.45	62.59	3.93	3.98	692	664[f]
	II													
$Mn(CO)_5$	H	H	C_6H_5	B	1	45	118.5–119	White	42.70	42.20	1.90	1.95	478	478
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	H	B	2.5	47	73–74	Yellow	40.66	40.26	2.62	2.25	384	384
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	CH_3	B'	0.5	85	123–124	Yellow	42.24	42.34	3.04	3.08	398	398
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	CH_3	CH_3	B'	1.7	25	96.5–98	Yellow	43.72	43.70	3.42	3.37	412	412
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	C_6H_5	B	0.5	84	118–119	Yellow	49.59	49.53	3.07	3.14	460	460
$\eta^5\text{-}C_5H_5Fe(CO)_2$	CH_3	H	H	B	0.5	18	105–106	Golden yellow	42.24	42.10	3.04	2.98	398	398
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	Cl	B	1.3	44	77–79	Yellow	*e*				418	418
$\eta^5\text{-}C_5H_5Mo(CO)_3$	H	H	C_6H_5	B	3	43	135.5–136.5	Yellow	45.47	45.42	2.67	2.68	530	530
$\eta^5\text{-}C_5H_5W(CO)_3$	H	H	H	B''	3	51	79–82	Yellow	31.14	31.15	1.87	1.86	540	540
$\eta^5\text{-}C_5H_5W(CO)_3$	H	H	CH_3	B	1	89	116–118	Yellow	32.51	32.41	2.18	2.15	554	554
$\eta^5\text{-}C_5H_5Fe(CO)L$[d]	H	H	H	C	4	22	161–162	Red	58.27	59.01	4.08	4.47	618	618
$\eta^5\text{-}C_5H_5Fe(CO)L$[d]	H	H	C_6H_5	C	2	40	145–146	Orange	62.27	62.59	4.21	4.37	694	694

[a] Methods A and B; see Experimental Section; methods B' and B'', same as B except in pentane and $CHCl_3$, respectively; method C, photochemical substitution as detailed in Experimental Section. [b] Calculated for the most common isotopic species. [c] Parent ion in the mass spectrum at 70 eV. [d] $L = P(C_6H_5)_3$. [e] Compound too unstable for commercial analyses; characterized spectroscopically. [f] Molecular ion not observed; highest *m/e* peak due to $M^+ - CO$.

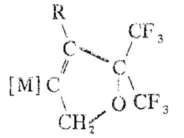
$\overline{C(CF_3)_2OC}H_2$ with SO_2. A solution of the title complex (0.16 g) in a mixture of liquid SO_2 (ca. 2 ml) and $CHCl_3$ (5 ml) was maintained at reflux for 6 hr. Evaporation to dryness afforded unreacted carbonyl complex as a red solid, 0.16 g.

Attempted Reaction of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{C{=}C(C_6H_5)}$-$\overline{C(CF_3)_2OC}H_2$ with HCl. To a solution of the title carbonyl complex (0.18 g) in 25 ml of acetone was added 0.25 ml of concentrated hydrochloric acid. The resulting solution was stirred for 24 hr and then neutralized with excess $NaHCO_3$. This was diluted with 35 ml of CH_2Cl_2, dried over $MgSO_4$, and filtered. Concentration of the filtrate yielded red crystals of unreacted carbonyl complex, 0.11 g.

Results and Discussion

Metal–Dihydrofuranato Derivatives. Transition metal–2-alkynyl complexes react with neat hexafluoroacetone or hexafluoroacetone in organic solvents to yield 1:1 adducts as indicated by elemental analyses and mass spectrometry. These products are crystalline solids that sublime at ca. 50° and 0.1 Torr. They are slightly soluble in pentane and very soluble in benzene, chloroform, and acetone. Some physical properties are listed in Table I.

By analogy with the known cycloaddition reactions of these same metal complexes with SO_2,[4] SO_3,[5] $(CN)_2C{=}C(CN)_2$,[6] and $ClSO_2NCO$,[7] inter alia, structure Ia is expected for the

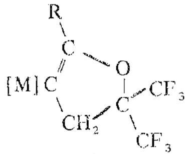


Ia

$[M] = Mn(CO)_5$, η^5-$C_5H_5Fe(CO)_2$; $R = CH_3, C_6H_5$

$[M] = \eta^5$-$C_5H_5Mo(CO)_3$; $R = C_6H_5$

isolated products. This structure is confirmed by the spectroscopic properties of the adducts (cf. Table II). The infrared carbonyl stretching frequencies are very similar to those reported for analogous cycloaddition products with different electrophiles[4–7] and for other, related metal–vinyl complexes.[20,21] In the proton NMR spectra of the dihydrofuranato derivatives, the CH_2O resonances are observed at τ 5.01–5.34 as generally broad singlets. The position of these signals is not consistent with the isomeric formulation Ib, since in



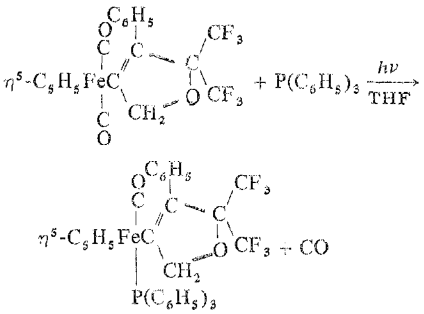
Ib

compounds containing a $CH_2C(CF_3)_2$ fragment the CH_2 resonance normally falls at τ 6.7–7.5.[19] In contrast, protons of the CH_2O moiety in the analogous SO_2[4] and SO_3[5] cycloadducts absorb at τ 4.28–4.94 and 4.84–5.14, respectively.

The broadness of the CH_2, and also of the $R = CH_3$ signals, is likely a result of spin–spin coupling between these nuclei, as well as with fluorine-19. The former coupling ($J_{CH_2-CH_3}$) is expected to be ca. 1.5–2.0 Hz[4–6] whereas the latter, long-range coupling (J_{H-F}) must be no greater than about 0.5 Hz as inferred from similar known hydrogen–fluorine coupling constants.[22] By comparison with the broad CH_2 and CH_3 resonances, the signals due to C_5H_5 appear as sharp singlets in these same spectra.

The fluorine-19 NMR spectra of these dihydrofuranato complexes show, as expected, only singlet resonances in the range of ϕ 73.6–75.6. Organic molecules containing a $C(CF_3)_2O$ linkage similarly display ^{19}F resonances near ϕ 75.[19]

The photochemical decarbonylation of an iron–dihydrofuranato complex in the presence of triphenylphosphine afforded a substituted monocarbonyl derivative, as shown in eq 4. The product contains a chiral metal, and this structural



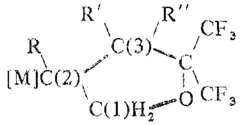
(4)

feature is reflected in the nonequivalence of the two CF_3 groups in its ^{19}F NMR spectrum (cf. Table II). The iron–carbon bond in this complex is unaffected by concentrated hydrochloric acid and by sulfur dioxide, thus further underscoring the stability of transition metal–vinyl linkages toward electrophilic cleavage.[4a]

Metal–Tetrahydrofuranato Derivatives. Transition metal–2-propenyl and –2-alkenyl complexes that bear alkyl or aryl substituents at the 3 carbon react with hexafluoroacetone in organic solvents to yield 1:1 adducts. However, for unknown reasons, no reaction was observed between these same complexes and neat hexafluoroacetone.

The isolated adducts, whose formulation is based on elemental analyses and mass spectral data (Table I), are crystalline solids that sublime at ca. 50° and 0.1 Torr. Their solubility properties are similar to those of the dihydrofuranato analogs.

The spectroscopic properties, given in Table II, support structure IIa for these complexes. Thus the infrared carbonyl



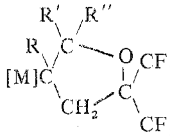
IIa

$[M] = Mn(CO)_5$, η^5-$C_5H_5Mo(CO)_3$; $R = R' = H$, $R'' = C_6H_5$

$[M] = \eta^5$-$C_5H_5Fe(CO)_2$; $R = H$, $R' = R'' = CH_3$; $R = R' = H$, $R'' = H, CH_3, C_6H_5, Cl$

$[M] = \eta^5$-$C_5H_5W(CO)_3$; $R = R' = H$, $R'' = H, CH_3$

stretching frequencies fall in the range reported for analogous transition metal–alkyl derivatives.[6,7,23,24] As for the dihydrofuranato complexes, the position of the CH_2O proton resonances is consistent with structure IIa but not with IIb.[19]



IIb

With the exception of sharp singlets for the C_5H_5 protons, the ^1H NMR resonances are quite broad owing to hydrogen–hydrogen and hydrogen–fluorine coupling. Hence they are of limited assistance in the elucidation of structure.

The ^{19}F NMR spectra of the complexes under discussion are each composed of two quartets of equal intensity in the region ϕ 71.4–81.0, with $J_{CF_3-CF_3} = 8.5$–10.3 Hz. Such spectra are characteristic of compounds containing nonequivalent CF_3 groups in a $C(CF_3)_2$ moiety.[13,25] Significantly, the chemical shift difference ($\Delta\phi$) is less than 1.0 ppm for the complexes IIa with $R' = R''$ and more than 3.3 ppm for those with $R' \neq R''$. In the former compounds, the asymmetric center nearest to $C(CF_3)_2$ is the carbon bonded to the metal (C(2); cf. IIa). However, in the latter compounds, the nearest asymmetric center is one bond closer to the $C(CF_3)_2$ fragment (C(3); cf. IIa). A smaller difference between the two values

Table II. Infrared ν_{CO} Absorptions and ^1H and ^{19}F NMR Spectra of Complexes of the Type $[M]C{=}C(R)C(CF_3)_2OCH_2$ (I) and $[M]C(R)C(R')(R'')C(CF_3)_2OCH_2$ (II)

Complex					^1H NMR, τ[b]					^{19}F NMR for CF_3	
[M]	R	R′	R″	Ir, ν_{CO},[a] cm^{-1}	C_5H_5	OCH_2	R	R′	R″	ϕ, ppm[c]	J, Hz
	I										
$Mn(CO)_5$	CH_3			2121 w, 2059 vw, 2031 vs, 2012 m		5.16 s, br	7.98 s, br			75.5 s	
$Mn(CO)_5$	C_6H_5			2120 w, 2032 vs, 2025 vs, 2008 m–s		5.01 s	2.71 s			75.5 s	
η^5-$C_5H_5Fe(CO)_2$	CH_3			2033 vs, 1984 vs	5.07 s	5.34 s, br	8.04 s, br			75.6 s	
η^5-$C_5H_5Fe(CO)_2$	C_6H_5			2033 vs, 1984 vs	5.35 s	5.16 s	2.68 m			74.1 s	
η^5-$C_5H_5Mo(CO)_3$	C_6H_5			2038 s, 1972 m–s, 1952 vs	4.82 s	5.13 s	2.72 s			73.6 s	
η^5-$C_5H_5Fe(CO)L$[d]	C_6H_5			1948 vs[e]	5.83 d[g]	5.64 s, br	2.97 m			74.0 q, 72.9 q	9.0
	II										
$Mn(CO)_5$	H	H	C_6H_5	2116 w, 2022 vs, 2004 m		6.6–5.2 m, br	8.0–7.2 m, br		2.68 s	74.7 q, 71.4 q	9.0
η^5-$C_5H_5Fe(CO)_2$	H	H	H	2020 vs, 1972 vs	5.18 s	6.5–5.6 m, br	8.1–7.3 m, br			77.6 q, 76.9 q	8.7
η^5-$C_5H_5Fe(CO)_2$	H	H	CH_3	2022 s, 2019 sh, 1973 s, 1968 s	5.19 s	6.5–5.6 m, br	8.2–7.8 m, br		8.65 d[h]	76.5 q, 72.2 q	8.5
η^5-$C_5H_5Fe(CO)_2$	H	CH_3	CH_3	2016 vs, 1966 vs	5.15 s	6.04 s, br, 5.88 s, br	7.3–6.8 m, br	9.0–8.5 m, br		81.0 q, 80.1 q	9.2
η^5-$C_5H_5Fe(CO)_2$	H	H	C_6H_5	2023 s, 2017 s, 1972 s, 1966 s	5.38 s	6.6–5.6 m, br	7.4–6.9 m, br		2.73 s	74.8 q, 71.1 q	9.3
η^5-$C_5H_5Fe(CO)_2$	CH_3	H	H	2018 vs, 1968 vs	5.18 s	5.89 s	8.63 s	7.53 s, br		76.4 q, 76.0 q	10.3
η^5-$C_5H_5Fe(CO)_2$	H	H	Cl	2028 s, 2023 m, 1984 m, 1978 vs, 1972 m[f]	5.10 s, 5.06 s[f]	6.5–5.6 m, br	7.9–6.8 m, br	5.6–4.8 m, br		j	
η^5-$C_5H_5Mo(CO)_3$	H	H	C_6H_5	2028 s, 1960 w, 1951 sh, 1944 s	5.01 s	6.25–5.25 m, br	7.2–6.6 m, br		2.68 s	74.4 q, 70.4 q	9.4
η^5-$C_5H_5W(CO)_3$	H	H	H	2027 m, 1946 m, 1936 s	4.52 s	6.3–5.6 m, br	7.9–7.3 m, br			j	
η^5-$C_5H_5W(CO)_3$	H	H	CH_3	2025 s, 1942 sh, 1934 vs	4.52 s	6.4–5.7 m, br	7.8–7.1 m, br		8.71 s	76.2 q, 72.2 q	8.8
η^5-$C_5H_5Fe(CO)L$[d]	H	H	H	1930 vs[e]	5.67 s, br	5.6 m, br	8.0–7.1 m, br			j	
η^5-$C_5H_5Fe(CO)L$[d]	H	H	C_6H_5	1930 vs[e]	5.73 t[i]	5.5–5.2 m, br	8.0–7.1 m, br 6.8–6.4 m, br		2.9 m	76.5 q, 74.9 q,[k] 74.7 q[k]	9.7

[a] In pentane solution unless otherwise indicated. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] In $CDCl_3$ solution. All signals integrate for the proper number of protons. Phenyl protons of $P(C_6H_5)_3$ are not tabulated. Abbreviations: s, singlet; d, doublet; t, triplet; m, complex multiplet; br, broad. [c] Relative to $CFCl_3$, taking $\phi_{C_6H_5CF_3}$ to be 63.7 ppm. Quartets are of equal intensity unless otherwise indicated. [d] $L = P(C_6H_5)_3$. [e] In $CHCl_3$ solution. [f] One absorption may be due to an extraneous material. [g] $J_{H-P} = 1.3$ Hz. [h] $J = 6.5$ Hz. [i] Likely due to overlap of two doublets, $J_{H-P} = 1.2$ Hz. [j] Not measured. [k] Observed as an approximate 1:3:4:3:3:1 sextet. The combined signal is as intense as that at 76.5 ppm.

of $\Delta\phi$ would be expected for the isomeric structure IIb.

The iron dicarbonyl complexes of structure IIa ([M] = η^5-$C_5H_5Fe(CO)_2$) with R' = R'' (H or CH_3) exhibit the expected two infrared ν_{CO} bands in pentane solution. However, when R' (H) $\neq$ R'' (CH_3, C_6H_5, or Cl), a pair of doublets of approximately equal intensity is observed in pentane, hexane, or cyclohexane, with the average separation between the high- and low-frequency components of these doublets being 5 cm^{-1}. In chloroform and other polar solvents, all complexes IIa show two, now broader, ν_{CO} absorptions.

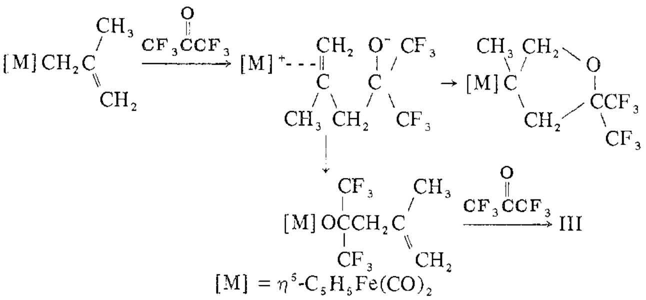
Two possible *a priori* explanations present themselves for this phenomenon. (1) When R' $\neq$ R'', there are two pairs of enantiomers owing to the presence of two chiral centers in IIa, C(2) and C(3). Each pair would have its distinct set of ν_{CO} absorptions. (2) Both pairs of enantiomers may, but need not,[27] be present. If both are present, then they have identical ν_{CO} spectra, and the observed four-band pattern arises from conformational isomerism about the iron–carbon bond[29] and/or within the tetrahydrofuranato ligand. Conformational isomerism about the iron–carbon bond is well known for complexes of the type η^5-$C_5H_5Fe(CO)_2X$ (X = $SiCl_2CH_3$, η^1-C_5H_5, SO_2CH_3, $CH_2C_{10}H_7$, inter alia).[30] In the present case it would curiously arise only when R' $\neq$ R'', i.e., when diastereomers are either present or possible.

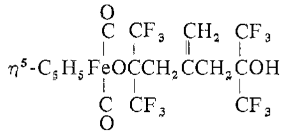
In an attempt to elucidate the observed phenomenon, efforts were made to achieve at least partial separation of the possible diastereomers of these complexes by vacuum sublimation, fractional crystallization, and column chromatography. They were all unsuccessful, thus neither supporting nor necessarily refuting the presence of diastereomers. Likewise, all attempts at altering the relative population of the possible conformers when R' $\neq$ R'' by varying the temperature appeared unsuccessful. The infrared ν_{CO} bands remained essentially unchanged in position and relative intensity over the temperature range of −78 to +25°. If the barrier to rotation about the iron–carbon bond were moderately low, the relative conformer population should have varied with the temperature (ν_{CO} band intensities change); if it were high, only one conformer should have been significantly populated in the first place (only two ν_{CO} bands). Hence no direct support could be obtained for the presence of either the diastereomers or the conformers.

A limited number of reactions of these cycloaddition complexes were investigated. The iron–carbon bond of IIa ([M] = η^5-$C_5H_5Fe(CO)_2$; R = R' = R'' = H and R = R' = H, R'' = CH_3) is cleaved with hydrogen chloride to afford η^5-$C_5H_5Fe(CO)_2Cl$. The fate of the organofluorine moiety was not determined. In contrast, IIa ([M] = η^5-$C_5H_5Fe(CO)_2$; R = R' = R'' = H) is unaffected by SO_2 at reflux. This inertness may be a result of the bulkiness of the tetrahydrofuranato ligand which would prevent backside attack of SO_2 at C(2).[23] Under photochemical conditions, the iron dicarbonyl complexes IIa having R = R' = R'' = H and R = R' = H, R'' = C_6H_5 afford with triphenylphosphine the corresponding monocarbonyl derivatives, η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]\overline{CHCH(R'')C(CF_3)_2OCH_2}$.

The reaction of η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ with hexafluoroacetone in either pentane or dichloromethane affords two complexes in about 20% yield each. The cycloaddition product, η^5-$C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OCH_2}$, is one of the few known compounds that contain a transition metal–tertiary carbon bond.[6,9,31] A second, red product is also isolated, with some difficulty, from this reaction. The red color and the high carbonyl stretching frequencies (2065 and 2023 cm^{-1}) suggest that the iron in the η^5-$C_5H_5Fe(CO)_2$ moiety is bonded to an element more electronegative than carbon. The elemental analyses are consistent with a 1:2 adduct of the precursor 2-alkenyl complex and hexafluoroacetone. The compound decomposes readily in solution, but its proton NMR spectrum (cf. Experimental Section) shows a singlet C_5H_5 signal, two different CH_2 resonances, and a $=CH_2$ signal. The ^{19}F NMR spectrum suggests the presence of an equal number of two different types of CF_3 groups. The simplest structure consistent with these data is III.

Scheme I





η^5-$C_5H_5Fe(CO)_2OC(CF_3)_2CH_2C(=CH_2)CH_2C(CF_3)_2OH$

III

This structure receives support from the behavior of the red solid on pyrolysis. Heating the 1:2 adduct at 105° leads to the sublimation of white needles of the known[19] $HOC(CF_3)_2CH_2C(=CH_2)CH_2C(CF_3)_2OH$. This organofluorine compound is considered to be formed through cleavage of the Fe–O bond of III followed by addition of hydrogen to the organic fragment. If the 1:2 adduct had a structure other than III and if it decomposed to methylpropene and hexafluoroacetone on pyrolysis, then combination of these latter species in a 1:2 ratio would have afforded two or three isomeric products $C_{12}H_8F_{12}O_2$.[19] It is noteworthy that thermal decomposition of η^5-$C_5H_5Fe(CO)_2\overline{C(CH_3)CH_2C(CF_3)_2OCH_2}$ affords some $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ but no detectable $C_{12}H_8F_{12}O_2$.

Conclusions

The observed behavior of hexafluoroacetone toward transition metal-2-alkenyl and -2-alkynyl complexes confirms the generality of this type of (3 + 2) cycloaddition reaction. Moreover, and as previously noted for chlorosulfonyl isocyanate,[7a] the reaction of η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ differs from that of the other iron 2-alkenyls investigated. Here, a product of insertion into the iron–carbon bond is obtained in addition to the product of cycloaddition. A mechanistic rationalization of this behavior is depicted in Scheme I. The different behavior of η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ may be attributed to a greater lability of the iron–olefin bond in the dipolar intermediate which favors dissociation and thence apparent insertion. This point was discussed in some detail earlier.[7a]

A number of structurally similar cycloaddition products have now been synthesized from transition metal-2-alkynyl complexes and various electrophiles, thus allowing some correlations to be made in their properties. One of such correlations is given in Table III. There various cycloaddition products derived from η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ are listed in the order of increasing values of their ν_{CO}. Although these frequencies span a narrow range of 10–11 cm^{-1}, they were obtained by the same operator and under identical conditions. Therefore the trend must be considered significant.

The higher values of ν_{CO} reflect stronger electron-withdrawing characteristics of the organic ring system. This in turn appears to be related to the electrophilic nature of E in the EN fragment (cf. eq 1), whose properties, unlike those

Table III. Infrared ν_{CO} Absorptions of η^5-$C_5H_5Fe(CO)_2\overline{C{=}C(C_6H_5)ENCH_2}$

$E{=}N$	ν_{CO},[a] cm^{-1}	Ref[b]
$C_6H_5N{=}S(O)$	2029, 1978	*c*
$(C_6H_5)_2C{=}C{=}O$	2029, 1979	*d*
$(CF_3)_2C{=}O$	2033, 1982	This work
$(O)S{=}O$	2034, 1983	4a
p-$CH_3C_6H_4S(O)_2N{=}S(O)$	2035, 1985	*e*
$(O)_2S{=}O$	2038, 1988	5
$ClSO_2N{=}C{=}O$	2038, 1989	7a
$(CN)_2C{=}C(CN)_2$	2039, 1989	6

[a] In $CHCl_3$ solution using matched 0.05-mm NaCl cells. [b] Synthesis. [c] P. W. Robinson and A. Wojcicki, *Chem. Commun.*, 951 (1970). [d] Y. Yamamoto, unpublished results. [e] D. W. Lichtenberg, Ph.D. Thesis, The Ohio State University, 1973.

of N, can be transmitted to the metal through the carbon–carbon double bond. Interestingly, $(CN)_2C{=}C(CN)_2$, $ClSO_2NCO$, and SO_3, known to be among the strongest electrophiles, not only show the highest values of ν_{CO} in their cycloadducts but also appear to react most rapidly with the metal–2-alkynyl complexes.[6,5a,7a]

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $[Mn(CO)_5]\overline{C{=}C(CH_3)C(CF_3)_2OCH_2}$, 54657-47-5; $[Mn(CO)_5]\overline{C{=}C(C_6H_5)C(CF_3)_2OCH_2}$, 54657-48-6; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{C{=}C(CH_3)C(CF_3)_2OCH_2}$, 54657-49-7; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{C{=}C(C_6H_5)C(CF_3)_2OCH_2}$, 54657-50-0; $[\eta^5$-$C_5H_5Mo(CO)_3]\overline{C{=}C(C_6H_5)C(CF_3)_2OCH_2}$, 54774-69-5; $[\eta^5$-$C_5H_5Fe(CO)(P(C_6H_5)_3)]\overline{C{=}C(C_6H_5)C(CF_3)_2OCH_2}$, 54657-51-1; $[Mn(CO)_5]\overline{CHCH(C_6H_5)C(CF_3)_2OCH_2}$, 54724-96-8; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{CHCH_2C(CF_3)_2OCH_2}$, 54657-44-2; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{CHCH(CH_3)C(CF_3)_2OCH_2}$, 54657-45-3; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{CHC(CH_3)_2C(CF_3)_2OCH_2}$, 54657-46-4; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{CHCH(C_6H_5)C(CF_3)_2OCH_2}$, 54657-24-8; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{C(CH_3)CH_2C(CF_3)_2OCH_2}$, 54657-25-9; $[\eta^5$-$C_5H_5Fe(CO)_2]\overline{CHCH(Cl)C(CF_3)_2OCH_2}$, 54657-26-0; $[\eta^5$-$C_5H_5Mo(CO)_3]\overline{CHCH(C_6H_5)C(CF_3)_2OCH_2}$, 54657-27-1; $[\eta^5$-$C_5H_5W(CO)_3]\overline{CHCH_2C(CF_3)_2OCH_2}$, 54657-28-2; $[\eta^5$-$C_5H_5W(CO)_3]\overline{CHCH(CH_3)C(CF_3)_2OCH_2}$, 54657-29-3; $[\eta^5$-$C_5H_5Fe(CO)(P(C_6H_5)_3)]\overline{CHCH_2C(CF_3)_2OCH_2}$, 54657-30-6; $[\eta^5$-$C_5H_5Fe(CO)(P(C_6H_5)_3)]\overline{CHCH(C_6H_5)C(CF_3)_2OCH_2}$, 54657-31-7; η^5-$C_5H_5Fe(CO)_2C_4H_7{\cdot}2(CF_3)_2CO$, 54657-32-8; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; η^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, 31781-60-9; HCl, 7647-01-0; PPh_3, 603-35-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, 31798-46-6; hexafluoroacetone, 684-16-2.

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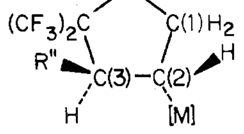
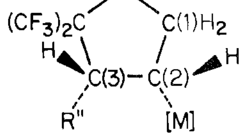
(26) When R'' = Cl, stability of the cycloadduct in solution is much lower. Thus we suspect that an additional ν_{CO} infrared band and one of the C_5H_5 proton resonances (cf. Table II) may be due to an impurity. Similar lower stability of complexes derived from reactions of transition metal-3-chloro-2-propenyl complexes with SO_2 was noted earlier.[17,18]

(27) Rosenblum[7b] has recently demonstrated that the cycloaddition of tosyl isocyanate to 2-cycloalkenyliron complexes affords the trans product exclusively. Such retention of stereochemistry about the C(2)–C(3) bond of the allyl fragment is the expected consequence of the proposed[9] two-step mechanism for the reaction of metal 2-alkenyls with electrophiles. Previously Merour[28] has shown that η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHR''$ complexes exist either totally (R'' = C_6H_5) or predominantly (R'' = CH_3, 67–75%) as the trans isomers, regardless of the geometry of the precursor allyl halides. Therefore, one expects the formation of trans tetrahydrofuranato derivatives either exclusively or predominantly. These trans isomers are also sterically more favored than their cis analogs.



trans



cis

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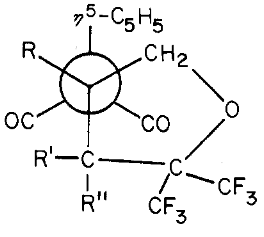

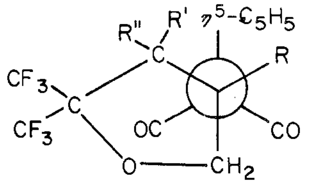

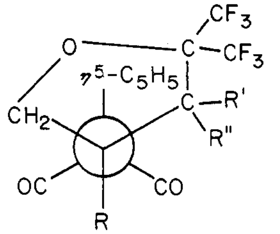

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