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Cycloaddition Reactions of Transition Metal–2-Alkynyl Complexes with Diphenylketene, *t*-Butylcyanoketene, *N*-Sulfinylaniline, and *N*-Sulfinyl-*p*-toluenesulfonamide

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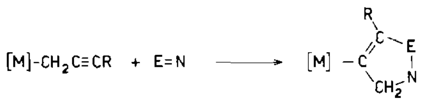
The reactions of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ *(R =* CH_3, C_6H_5, *and* $CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$*),* η^5-C_5H_5-$Mo(CO)_3CH_2C{\equiv}CC_6H_5$, *and* $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ *(*$[M]CH_2C{\equiv}CR$*) with the ketenes* $(C_6H_5)_2C{=}C{=}O$ *and* $(t$-$C_4H_9)(CN)C{=}C{=}O$ *and with the* N-*sulfinyl compounds* $C_6H_5N{=}S{=}O$ *and* p-$CH_3C_6H_4SO_2N{=}S{=}O$ *result in the formation of (3 + 2) cycloadducts of the reactants. The respective products of these reactions are* $[M]C{=}C(R)C(O)C(C_6H_5)_2CH_2$, $[M]C{=}C(R)C(O)C(t$-$C_4H_9)(CN)CH_2$, $[M]C{=}C(R)S(O)N(C_6H_5)CH_2$, *and* $[M]C{=}C(R)S(O)N(SO_2C_6H_4$-$CH_3)CH_2$. *These structures have been elucidated on the basis of infrared,* ^1H *NMR, and* ^{13}C *NMR spectroscopic data. No reactions were observed between* η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ *and* $C_2H_5O_2$-$CN{=}NCO_2C_2H_5$ *and between* η^5-$C_5H_5Fe(CO)_2R$ *(R =* CH_3 *and* $CH_2C_6H_4OCH_3$-p*) and the two ketenes.*

Introduction

It has been shown in this [1, 2] and other laboratories [3–5] that transition metal–2-alkynyl complexes undergo reactions with various electrophiles such as SO_2, SO_3, $ClSO_2NCO$, $(CF_3)_2CO$, and $(CN)_2C{=}C(CN)_2$ (E=N) to yield (3 + 2) cycloaddition products.



In order further to ascertain the scope of such electrophilic additions we have extended our investigation to four heterocumulenes: $(C_6H_5)_2C{=}C{=}O$, $(t$-$C_4H_9)(CN)C{=}C{=}O$, $C_6H_5N{=}S{=}O$, and *p*-$CH_3C_6H_4SO_2N{=}S{=}O$.

Only few reactions of ketenes with organometallic compounds of transition metals are known which do not result in decarbonylation or deoxygenation of the ketene. Insertion of ketene into the Mn–H bond in $Mn(CO)_5H$ is reported [6] to afford $Mn(CO)_5COCH_3$. Diphenylketene replaces a carbonyl group in η^5-$RC_5H_4Mn(CO)_3$ (R = H and CH_3) [7] and inserts into one Ni–CH_3 bond in $(CH_3)_2Ni[P(C_6H_5)_3]_3$ [8]. Reaction between $(\eta^5$-$C_5H_5)_2Ni$ and $(CH_3)_2C{=}C{=}O$ results in (2 + 2) cycloaddition to the C_5H_5 ring of one molecule of the ketene and insertion into a Ni–C bond of another [9].

N-Sulfinylamines and *N*-sulfinylsulfonamides have not been investigated with respect to their behavior toward organometallic compounds of transition metals***.

Presented herein are the results of our study on reactions of various metal-2-alkynyl complexes with the four heterocumulenes. Certain aspects of this work were communicated earlier [10]. Described in this paper are also attempted reactions of iron–2-alkynyl and –alkyl complexes with $C_2H_5O_2CN{=}NCO_2C_2H_5$ and of iron–2-alkenyl and –alkyl complexes with $(C_6H_5)_2C{=}C{=}O$ and $(t$-$C_4H_9)(CN)C{=}C{=}O$.

Experimental

General Procedures

All reactions were conducted under an atmosphere of nitrogen. Florisil (60–100 mesh), from Fisher, and Ventron alumina, deactivated with distilled H_2O (6–10%), were used in chromatographic separations and purifications. Melting points were measured *in vacuo* on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements

^1H NMR spectra were recorded on Varian Associates A-60 and A-60A spectrometers using tetramethylsilane as a reference. ^{13}C NMR spectra were obtained on a Bruker HX-90 spectrometer at 22.625

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***However reactions of *N*-sulfinylanilines and *N*-sulfinylsulfonamides with platinum(II) and iridium(I) complexes have been examined; see D. M. Blake and J. R. Reynolds, *J. Organomet. Chem., 113*, 391 (1976).

MHz in a Fourier transform mode by Drs. J. P. Williams and C. E. Cottrell. Infrared (ir) spectra were recorded on a Beckman IR-9 spectrophotometer or a Perkin–Elmer Model 337 spectrophotometer. Mass spectral measurements were made at 70eV on an A.E.I. Model MS-9 spectrometer by Mr. C. R. Weisenberger.

Materials

The ketenes $(C_6H_5)_2C{=}C{=}O$ [11] and $(t\text{-}C_4H_9)(CN)C{=}C{=}O$ (in benzene solution) [12] and the *N*-sulfinyl compounds $C_6H_5N{=}S{=}O$ [13] and $p\text{-}CH_3C_6H_4SO_2N{=}S{=}O$ [14] were prepared by the literature methods. Diethyl azodicarboxylate, $C_2H_5O_2CN{=}NCO_2C_2H_5$, was procured from Aldrich Chemical Co. and used as received. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen immediately before use. Other commercially procured solvents and chemicals were reagent grade or equivalent quality and were used without further purification.

The complexes $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ (R = CH_3, [15], C_6H_5, [16], and $CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ [17]), $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ [16], $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ [16], $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ [18], $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ [19], and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C_6H_4OCH_3\text{-}p$ [20], were prepared according to published methods.

Reactions of Metal–2-Alkynyl Complexes with Diphenylketene

In a typical reaction, 0.87 g (4.5 mmol) of $(C_6H_5)_2C{=}C{=}O$ in 5 ml of benzene was added to a solution of 0.73 g (3.2 mmol) of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ in 25 ml of CH_2Cl_2 at –40 °C. The resulting mixture was allowed to warm to room temperature.

After 5 hr of stirring the solution was concentrated under reduced pressure and chromatographed on alumina. Elution with 1/3 pentane/CH_2Cl_2 developed a yellow band which was removed. Solvent was evaporated off and the residue was crystallized from CH_2Cl_2/pentane to afford 0.34 g of a 1:1 adduct as yellow crystals. Work-up of the mother liquor gave an additional 0.62 g (71% total yield) of the product.

The reactions of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ with $(C_6H_5)_2C{=}C{=}O$ were conducted similarly. Yields, analytical data, and physical properties of all diphenylketene-containing complexes prepared herein are provided in Table I.

Attempted Reactions of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$, and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C_6H_4OCH_3$-p with Diphenylketene

A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (0.80 g, 3.3 mmol) and $(C_6H_5)_2C{=}C{=}O$ (0.97 g, 5.0 mmol) in 20 ml of CH_2Cl_2 was stirred for 21 hr at room temperature. Solvent was removed under reduced pressure and the yellow-orange oil was chromatographed on alumina. Elution with pentane led to a recovery of 0.68 g (85%) of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$.

Similarly no reaction was observed at room temperature in CH_2Cl_2 solution between the $\eta^5\text{-}C_5H_5Fe(CO)_2R$ (R = CH_3 and $CH_2C_6H_4OCH_3\text{-}p$) and $(C_6H_5)_2C{=}C{=}O$.

Reactions of Metal–2-Alkynyl Complexes with t-*Butylcyanoketene*

In a representative reaction, $(t\text{-}C_4H_9)(CN)C{=}C{=}O$ (~2.5 mmol) in dry benzene (10 ml) was added dropwise with stirring to a solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.44 g, 1.5 mmol) in dry benzene (20 ml) at room temperature. After the mixture had been stirred for 3 hr at room temperature, solvent was removed under reduced pressure. The resulting yellow–brown oil was chromatographed on alumina. Elution with 1/1 pentane/CH_2Cl_2 afforded unreacted $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and then elution with CH_2Cl_2 gave an orange solution of the product. Removal of the solvent and treatment of the resulting semisolid with pentane (20 ml) yielded the product as a yellow solid (0.25 g, 40%).

Reactions of each of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$, and $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ with $(t\text{-}C_4H_9)(CN)C{=}C{=}O$ were carried out in a similar manner. Yields, analytical data, and physical properties of all new products are furnished in Table I.

Attempted Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ with t-*Butylcyanoketene*

To a solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ (0.50 g, 2.6 mmol) in dry benzene (20 ml) at room temperature was added dropwise with stirring $(t\text{-}C_4H_9)(CN)C{=}C{=}O$ (~0.30 mmol) in dry benzene (10 ml). The mixture was stirred for 2 hr at room temperature, solvent was removed, and the residue was chromatographed on alumina. Only unreacted $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ and ketene dimer were recovered.

Reactions of Metal–2-Alkynyl Complexes with N-*Sulfinylaniline*

To freshly distilled $C_6H_5N{=}S{=}O$ (1.2 g, 0.86 mmol) was added $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ (1.15 g, 0.500 mmol) and the solution was stored for 48 hr at room temperature resulting in the formation of a brown precipitate. The excess $C_6H_5N{=}S{=}O$ was then decanted off and the precipitate was washed with CH_2Cl_2/pentane. It was recrystallized from toluene-pentane to give 0.34 g (18%) of a yellow solid.

The reaction between $C_6H_5N{=}S{=}O$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ was conducted analogously for 70 hr with similar results. However, no precipitation was observed after C_6H_5-

TABLE I. Yields, Analytical Data, and Physical Properties of New Complexes: $[M]\overline{C{=}C(R)C(O)C(C_6H_5)_2C}H_2$ (I), $[M]\overline{C{=}C(R)C(O)C(t\text{-}C_4H_9)(CN)C}H_2$ (II), $[M]\overline{C{=}C(R)S(O)N(C_6H_5)C}H_2$ (III), and $[M]\overline{C{=}C(R)S(O)N(SO_2C_6H_4CH_3)C}H_2$ (IV).

Complex			Yield, %	Mp, °C	Color	Analysis, %						Mol. wt.	
No.	[M]	R				C		H		N		Calcd	Found[a]
						Calcd	Found	Calcd	Found	Calcd	Found		
Type I													
1	η^5-$C_5H_5Fe(CO)_2$	CH_3	71	188–192 (dec)	yellow	70.77	70.87	4.75	4.88			424	424
2	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	68	165–167	yellow	74.09	74.16	4.56	4.60			486	486
3	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	34	~83 (dec)	yellow	64.03	64.50	4.03	4.28			d	
Type II													
4	η^5-$C_5H_5Fe(CO)_2$	CH_3	45	145–146 (dec)	yellow	61.21	61.17	5.42	5.26	3.97	3.88	353	353
5	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	40	187–188 (dec)	yellow	66.52	66.27	5.10	5.10			415	415
6	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	18	163–165 (dec)	yellow	56.75	56.53	4.38	4.41			529	529
7	η^5-$C_5H_5Mo(CO)_3$	C_6H_5	37	143–145 (dec)	yellow	59.64	59.56	4.38	4.28			d	
Type III													
8	η^5-$C_5H_5Fe(CO)_2$	CH_3	18	97–98 (dec)	yellow	55.30	55.2	4.10	4.2	3.79	3.8	369	369
9	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	30	80–83 (dec)	brown[b]	61.27	58.0	3.97	3.7	3.25	2.8	431	431
10	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	25	169–170 (dec)	yellow	52.88	53.0	3.51	3.5	2.57	2.7	d	
Type IV													
11	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	66	65–75	yellow	c						d	
12	$Mn(CO)_5$	C_6H_5	85	110–115	cream	c						d	

[a] Parent ion in the mass spectrum. [b] Impure. [c] Not analyzed; see Experimental. [d] Molecular ion not observed; compound decomposes in the mass spectrometer.

N=S=O (~1 ml) and η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.82 g) had been stored for 90 hr. This mixture was then treated with 5 ml of benzene and poured into 50 ml of pentane to afford a brown precipitate. Recrystallization was effected from benzene/pentane; however, elemental analyses on the recrystallized sample were poor. Yields, analytical data, and physical properties of the three products are given in Table I.

Reactions of Metal–2-Alkynyl Complexes With N-*Sulfinyl*-p-*toluenesulfonamide*

A solution of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ (0.31 g, 1.0 mmol) in 2 ml of CH_2Cl_2 was added to p-$CH_3C_6H_4SO_2N{=}S{=}O$ (0.22 g, 1.0 mmol) in 2 ml of CH_2Cl_2 at room temperature. The mixture was stirred for 2 hr and then evaporated to dryness at *ca.* 0.1 Torr to give after washing with pentane 0.45 g (85%) of a cream solid. This solid was dissolved in a minimum amount of CH_2Cl_2 and eluted with acetone over a 2.5 X 10 cm column of Florisil. A light yellow solution was collected and concentrated to an oil. Treatment with pentane afforded a cream solid. From the ^1H NMR spectrum the solid appeared to be at least 90% pure. Further attempts at purification were unsuccessful.

The reaction of p-$CH_3C_6H_4SO_2N{=}S{=}O$ with η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ was conducted similarly to afford a yellow glass. All attempts at purification by crystallization or column chromatography invariably yielded similar glasses which, from the ^1H NMR spectra, appeared to contain appreciable amounts of impurities.

Yields and physical properties of the two products are given in Table I. No analytical data were obtained because of the impure nature of the samples isolated.

Attempted Oxidation of $Mn(CO)_5C{=}C(C_6H_5)S(O)N(SO_2C_6H_4CH_3)CH_2$

A 1.3 g sample of the title compound in 10 ml of glacial acetic acid was treated with 0.5 g of $KMnO_4$ in 5 ml of H_2O. The resulting brown suspension was extracted twice with 50 ml portions of CH_2Cl_2 and the CH_2Cl_2 layer was neutralized with $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent gave 0.1 g of a white solid which was identified as unreacted title compound. There was no evidence for $Mn(CO)_5C{=}C(C_6H_5)S(O)_2N(SO_2C_6H_4CH_3)CH_2$.

Attempted Reactions of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ *and* η^5-$C_5H_5Fe(CO)_2CH_2C_6H_4OCH_3$-p *with Diethyl Azodicarboxylate*

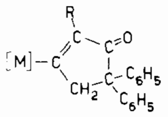
To a solution of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ (0.60 g, 2.6 mmol) in 20 ml of CH_2Cl_2 at room temperature was added $C_2H_5O_2CN{=}NCO_2C_2H_5$ (0.87 g, 5.0 mmol) in 5 ml of benzene. The mixture was stirred for 28 hr, solvent was removed, and the residue was chromatographed on alumina. Elution with pentane and benzene afforded unreacted starting materials and some $[\eta^5$-$C_5H_5Fe(CO)_2]_2$.

The reaction between η^5-$C_5H_5Fe(CO)_2CH_2C_6H_4OCH_3$-$p$ and $C_2H_5O_2CN{=}NCO_2C_2H_5$ was conducted similarly for 6 hr to yield only unreacted starting materials upon work-up.

Results and Discussion

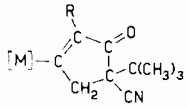
Transition metal–2-alkynyl complexes of the general formula η^5-$C_5H_5M(CO)_xCH_2C{\equiv}CR$ (M = Fe, x = 2 and M = Mo, x = 3) react at room temperature with each of the ketenes $(C_6H_5)_2C{=}C{=}O$ and $(t$-$C_4H_9)(CN)C{=}C{=}O$ to yield 1:1 adducts of the reactants as indicated by elemental analyses and mass spectrometry. These products are air-stable yellow solids that are soluble in organic solvents.

The proposed structures of the diphenylketene- and *t*-butylcyanoketene-derived products, I and II, respectively, are based on the spectroscopic data set out in Table II.



I

1 [M] = η^5-$C_5H_5Fe(CO)_2$, R = CH_3
2 [M] = η^5-$C_5H_5Fe(CO)_2$, R = C_6H_5
3 [M] = η^5-$C_5H_5Fe(CO)_2$, R = $CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$



II

4 [M] = η^5-$C_5H_5Fe(CO)_2$, R = CH_3
5 [M] = η^5-$C_5H_5Fe(CO)_2$ R = C_6H_5
6 [M] = η^5-$C_5H_5Fe(CO)_2$, R = $CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$
7 [M] = η^5-$C_5H_5Mo(CO)_3$, R = C_6H_5

Thus the infrared spectra show metal carbonyl stretching absorptions at frequencies similar to those reported for analogous cycloaddition products with various electrophiles [15, 21–25] and for other related metal–vinyl complexes [26, 27]. The ketonic $\nu(C{=}O)$ absorption is observed in the range 1681–1660 cm^{-1}, consistent with conjugation of the carbonyl group with the C=C linkage. The alternative cycloaddition structures I ALT and II ALT would be expected to exhibit a $\nu(C{=}O)$ band in the same range as five-membered-ring ketones, *i.e.* 1750–1740

TABLE II. Infrared and ^{1}H NMR Spectra of New Complexes: [M]$\overline{\text{C=C(R)C(O)C(C}_6\text{H}_5)_2\text{C}}\text{H}_2$ (I), [M]$\overline{\text{C=C(R)C(O)C(}t\text{-C}_4\text{H}_9\text{)(CN)C}}\text{H}_2$ (II), [M]$\overline{\text{C=C(R)S(O)N(C}_6\text{H}_5\text{)C}}\text{H}_2$ (III), and [M]$\overline{\text{C=C(R)S(O)N(SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{)C}}\text{H}_2$ (IV).

Complex			Ir, cm^{-1}				^{1}H NMR, τ[c]
No.	[M]	R	ν(C≡O)[a]	ν(C=O)[a]	ν(CN)[b]	ν(SO), ν(SN)[a]	
	Type I						
1	η^5-$C_5H_5Fe(CO)_2$	CH_3	2042vs, 1980vs	1670m			5.11s(C_5H_5), 6.24br(CH_2), 8.07br(CH_3)
2	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	2029vs, 1978vs	1673m			5.31s(C_5H_5), 6.13s(CH_2)
3	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	2038vs, 2005s, 1975vs, 1950s	1660m			5.13s(C_5H_5), 5.39s(C_5H_5), 6.53br(CCH_2C), 7.50br($FeCH_2$)
	Type II						
4	η^5-$C_5H_5Fe(CO)_2$	CH_3	2023vs, 1962vs[d]	1666s[d]	2229w[d]		4.72s(C_5H_5), 6.70q(J = 1.5Hz, CH_2), 8.10t (J = 1.5Hz, CH_3) 8.95s(C_4H_9)[f]
5	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	2030vs, 1978vs[e]	1681s[e]	2234w		5.27s(C_5H_5), 6.54, 6.70q_{AB} (J = 10Hz, CH_2), 8.87s(C_4H_9)
6	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	2030vs, 2008s, 1969vs, 1945s[e]	1675m[e]	2232w		5.07s(C_5H_5), 5.13s(C_5H_5), 6.96br(CCH_2C), 7.54, 7.84q_{AB} (J = 9Hz, $FeCH_2$), 8.92s(C_4H_9)
7	η^5-$C_5H_5Mo(CO)_3$	C_6H_5	2038s, 1966vs 1943vs[e]	1681m[e]	2226w		4.59s(C_5H_5), 6.57, 6.73q_{AB} (J = 17Hz, CH_2), 8.90s(C_4H_9)
	Type III						
8	η^5-$C_5H_5Fe(CO)_2$	CH_3	2022vs, 1974vs[b]			1052s, 925m[b]	4.92s(C_5H_5), 5.18, 5.52q_{AB} (J = 16Hz, CH_2), 7.64br(CH_3)
9	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	2029vs, 1978vs			1070s, 933m[b]	g
10	η^5-$C_5H_5Fe(CO)_2$	$CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$	2029vs, 1994s 1967vs, 1953s[b]			1068s, 925m[b]	4.85s(C_5H_5), 4.91s(C_5H_5), 5.41br(NCH_2), 7.68[h]($FeCH_2$)
	Type IV						
11	η^5-$C_5H_5Fe(CO)_2$	C_6H_5	2035vs, 1985vs			1360s, 1180s, 1105s, 985m, 915m[d]	5.34s(C_5H_5), 5.41s(CH_2), 7.59s(CH_3)[i]
12	$Mn(CO)_5$	C_6H_5	2128w, 2038vs, 2025sh			1330s, 1175s, 1115m, 990m, 920m[d]	4.43, 4.73q_{AB} (J = 14Hz, CH_2), 7.68s(CH_3)[j]

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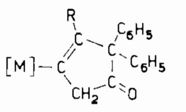
[a] In $CHCl_3$ solution unless otherwise indicated. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] As Nujol mull unless otherwise indicated. [c] In $CDCl_3$ solution unless otherwise indicated. C_6H_5 and C_6H_4 protons are not tabulated. Abbreviations: s, singlet; t, triplet; q, quartet; br, broad. [d] As KBr pellet. [e] In CH_2Cl_2 solution. [f] In $(CD_3)_2CO$ solution. [g] Not recorded. [h] Possibly an AB quartet with the outer peaks too weak to be observed. Separation of the inner peaks = 10 Hz. [i] Signals are broad and do not integrate exactly for the expected number of protons. [j] Signals resulting from the presence of impurities are not included.

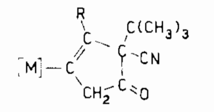
TABLE III. ^{13}C NMR Spectra of η^5-$C_5H_5Fe(CO)_2\overline{C{=}C(R)C(O)C(R')(R'')C}H_2$.

Chemical shift (δ)^a of complex		Assignment
($R = R' = R'' = C_6H_5$) **2**	($R = CH_3$, $R' = CN$, $R'' = t$-C_4H_9) **4**	
213.68	213.55	Fe–CO
206.04	203.85	$\rangle C{=}O$
199.85	193.88	Fe–C
156.69	149.88	$=C\langle$
144.78 138.65 130.28 128.25 128.08 126.90 126.23	–	C_6H_5
–	120.96	CN
85.76	85.57	C_5H_5
66.43	55.79	CH_2
62.66	54.28	$C(R')(R'')$
–	36.90	$C(CH_3)_3$
–	25.68	$(CH_3)_3$
–	13.86	$=C$–CH_3

^{a}Relative to tetramethylsilane. $CDCl_3$ used as solvent and lock.



I ALT



II ALT

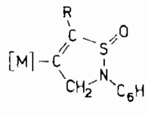
cm^{-1} [28]. The ν(CN) absorption for complexes II occurs with weak intensity at 2234–2226 cm^{-1}, as expected for this structure [29].

The ^1H NMR spectra of complexes **5** and **7** show the CH_2 resonance as an AB quartet owing to the presence of the chiral –$C(CN)(t$-$C_4H_9)$– carbon atom in the ketone ring. A similar nonequivalence of the methylene protons was noted earlier for analogous cycloaddition compounds derived from SO_2 [15] and from $CF_3(CN)C{=}C(CN)CF_3$ [25]. Curiously, this nonequivalence is not observed for complex **4**; however, the expected weak coupling between the protons of R = CH_3 and CH_2 [15, 21, 23, 24] is discernible (J = 1.5 Hz). The bimetallic complexes **3** and **6** each display two C_5H_5 and two CH_2 proton resonances in agreement with the proposed structures. Furthermore, in the spectrum of **6** the $FeCH_2$ protons appear as an AB quartet owing to the presence of a chiral carbon center in the ketone ring. However, similar nonequivalence is not discernible for the CCH_2C protons of **6** which give rise to a broad signal.

The ^{13}C NMR spectra of complexes **2** and **4**, given in Table III, provide further evidence for the assigned structures. The listed chemical shifts for the various carbon atoms occur in the expected ranges [30] and compare well with the corresponding data for several analogous (3 + 2) cycloaddition complexes [25].

The interaction of iron–2-alkynyl complexes of the formula η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ with *N*-sulfinylaniline for 48–90 hr at room temperature leads to the formation of 1:1 adducts of the two reactants as deduced from elemental analyses and mass spectra. Care must be exercised rigorously to exclude moisture since $C_6H_5N{=}S{=}O$ hydrolyzes readily to afford $C_6H_5NH_2$ and SO_2 [13]. The liberated SO_2 then rapidly undergoes (3 + 2) cycloaddition to the 2-alkynyl fragment of the η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ yielding the sultine complex III SULT ([M] = η^5-$C_5H_5Fe(CO)_2$). The isolated *N*-sulfinylaniline-containing products are yellow solids when pure and appear to be stable toward air.

These adducts are assigned structure III on the basis of the infrared and ^1H NMR spectroscopic data listed in Table II. Several features of the ^1H NMR

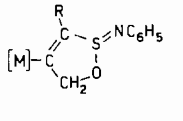


III

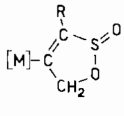
8 $[M] = \eta^5\text{-}C_5H_5Fe(CO)_2$, $R = CH_3$

9 $[M] = \eta^5\text{-}C_5H_5Fe(CO)_2$, $R = C_6H_5$

10 $[M] = \eta^5C_5H_5Fe(CO)_2$, $R = CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$



III ALT



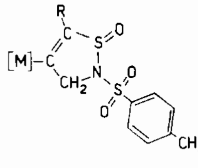
III SULT

spectra of **8** and **10** resemble closely those of the corresponding sultine complexes [15] the structure of one of which (III; $[M] = \eta^5\text{-}C_5H_5Fe(CO)_2$, $R = CH_3$) was elucidated crystallographically [31]. Thus the signals of the C_5H_5 protons of **8** and **10** and of the $FeCH_2$ protons of **10** occur at similar fields as those of the respective sultine counterparts [15]. Furthermore, complex **8**, just as its sultine analog, shows magnetic nonequivalence of the CH_2 protons, with a similar geminal coupling constant, J_{AB} [15]. In contrast, the chemical shifts of the NCH_2 protons of **8** and **10** are observed at appreciably higher fields (0.4–0.7 ppm) than those of the OCH_2 protons of the corresponding sultine complexes [15]. Similar higher chemical shifts were noted for the NCH_2 protons of the corresponding iron–Δ^3-pyrrolinone complexes, $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C{=}C(R)C(O)N(X)C}H_2$ [23]. These observations appear to support structure III for the *N*-sulfinylaniline-derived adducts; structure III ALT would be expected to show CH_2 proton chemical shifts more in accord with those of the corresponding sultine derivatives, III SULT.

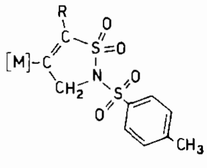
In the infrared spectra of complexes III $\nu(C{\equiv}O)$ absorptions occur in the same region as for other, similar (3 + 2) cycloaddition products [15, 21–25]. Additionally there are two prominent bands at 1070–1052 and 933–925 cm^{-1}. The absorption at 1070–1052 cm^{-1} is assigned to $\nu(S{=}O)$ by analogy with the corresponding absorption in the spectra of various *N*-substituted 3,6-dihydro-1,2-thiazine-1-oxides, $\overline{CH(R)C(R')=C(R'')CH(R''')N(X)S}{=}O$ (~1080 cm^{-1}), [13, 32], and of *N*-phenyl-*N*′,*N*′-dimethylsulfinyldiamidotrimethylstannane, $(CH_3)_3SnN(C_6H_5)S(O)N(CH_3)_2$ (1068 cm^{-1}) [33]. The other band, at 933–925 cm^{-1}, is best ascribed to $\nu(NS)$. The NS stretching frequency for a series of sulfinamides, $R_2NS(O)R$ [33, 34], and sulfonamides, $R_2NS(O)_2R$ [35], occurs in the range 930–870 cm^{-1}. Thus the infrared spectra further support structure III over III ALT for these 1:1 adducts.

Of additional significance is the observation of high stability of complexes III toward water. The alternative structure III ALT would be expected, by analogy with the behavior of related organic compounds [13, 14], to react with water yielding the corresponding metal–sultine complex (III SULT) and aniline.

The reaction of each of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ with $p\text{-}CH_3C_6H_4SO_2N{=}S{=}O$ yields complexes IV. These 1:1 adducts of the two reactants defied satisfactory purification and therefore were not characterized by elemental analyses. Furthermore, they underwent decomposition in the mass spectrometer at 110–150 °C, thus preventing the determination of their molecular weights. Nevertheless the spectroscopic properties listed in Table III appear to lend support to the assigned structure.



IV



IV OX

11 $[M] = \eta^5\text{-}C_5H_5Fe(CO)_2$, $R = C_6H_5$

12 $[M] = Mn(CO)_5$ $R = C_6H_5$

The infrared $\nu(C{\equiv}O)$ absorptions and the ^1H NMR chemical shifts of **11** and **12** are similar to those reported for various analogous (3 + 2) cycloaddition complexes [15, 21–25]. The infrared bands at 1360–1330 and 1180–1175 cm^{-1} and at 1115–1105 cm^{-1} are best assigned to $\nu(SO_2)$ and $\nu(S{=}O)$ modes, respectively, whereas those at 990–985 and 920–915 cm^{-1} likely arise from NS stretching. Structurally related 3,6-dihydro-*N*-arylsulfonyl-1,2-thiazine-1-oxides, $\overline{CH(R)C(R')=C(R'')CH(R''')N(SO_2C_6H_4X)S}{=}O$, show $\nu(SO_2)$ absorptions at 1350 and 1165 cm^{-1} and a $\nu(S{=}O)$ band at 1080 cm^{-1} [13], in agreement with the above assignment.

Further support for the proposed structure IV is provided by the behavior of *N*-sulfinylsulfonamides toward 1,3-dienes. These reactions, as well as those of various *N*-sulfinylamines, result in the formation of the corresponding *N*-substituted 3,6-dihydro-1,2-thiazine-1-oxide adducts, $\overline{CH(R)C(R')=C(R'')CH(R''')N(X)S}{=}O$ [13, 14]. The alternative mode of cycloaddition to give $\overline{CH(R)C(R')=C(R'')CH(R''')OS}{=}NX$ was not observed.

Since oxidation of 3,6-dihydro-*N*-arylsulfonyl-1,2-thiazine-1-oxides affords the corresponding *N*-arylsulfonyl-δ-sultams, $\overline{CH(R)C(R')=C(R'')CH(R''')N(SO_2C_6H_4X)S}(O)_2$ [14], an attempt was made also to oxidize **12** to IV OX ($[M] = Mn(CO)_5$, $R = C_6H_5$). However, only decomposition was observed when this manganese complex was treated with $KMnO_4$. It is of interest to note that oxidation with $KMnO_4$ of the sultine complex III SULT ($[M] = Mn(CO)_5$, $R = C_6H_5$) does yield the corresponding sultone, $Mn(CO)_5\overline{C{=}C(C_6H_5)S(O)_2OC}H_2$ [21].

Although no direct mechanistic evidence is available for the above-discussed (3 + 2) cycloaddition reactions of the ketenes and *N*-sulfinyl compounds with transition metal–2-alkynyl complexes, it is very probable that they proceed in two steps, via a dipolar metal–η^2-allene intermediate. Such a mechanism has been proposed for the reactions of these same metal–2-alkynyl complexes with various electrophiles and is discussed in some detail elsewhere [23, 25]. It accounts for the formation of complexes I and II rather than the alternative cycloadducts I ALT and II ALT, respectively, on the basis of charge distribution in the reacting ketenes, *i.e.*

$$R_2\overset{\delta^-}{C}=\overset{\delta^+}{C}=O$$

Likewise, the formation of complexes III and IV is in complete accord with this electrophilic two-step pathway. It is further of interest that when this mechanism cannot be operative, as is the case for metal–alkyl and –benzyl complexes, no reaction is observed between the η^5-$C_5H_5Fe(CO)_2R$ (R = CH_3 and $CH_2C_6H_4OCH_3$-*p*) and the two ketenes under investigation.

Finally, we wish to add that another dienophile, $C_2H_5O_2CN{=}NCO_2C_2H_5$, was shown in this study not to react with η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ at ambient temperatures. The observed lack of reactivity likely arises from the relatively poor electrophilic properties of this azodicarboxylate toward the coordinated 2-alkynyl fragment.

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