61618-13-1; Tm_3Zn^-, 63588-53-4; Bu_4NBr, 1643-19-2; $ZnBr_2$, 7699-45-8.

Supplementary Material Available: Infrared spectra of THF solutions of NaTm with varying amounts of $(n\text{-}Bu)_4NBr$ added are presented in Figure 1S; tables listing equilibrium concentrations determined from NMR spectral measurements in THF/Et_2O solutions of (a) $[\eta^5\text{-}C_5H_5(CO)_3Mo]$, (b) $\eta^5\text{-}C_5H_5(CO)_3MoZnBr$ and $Na[\eta^5\text{-}C_5H_5(CO)_3Mo]$, and (c) $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ and $n\text{-}Bu_4Br$ are given in Tables S-I, S-II, S-III, and S-IV (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **96**, 5427 (1974).
(2) (a) Abbreviations used in this paper: Tm = $\pi\text{-}C_5H_5(CO)_3Mo$; Bu = C_4H_9–; Et = C_2H_5–; Me = CH_3–; THF = tetrahydrofuran; DMF = dimethylformamide; Me_2SO = dimethyl sulfoxide. (b) Standard errors for the last digits are given in parentheses.
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Stereochemistry of the Cycloaddition Reaction of 1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene with Transition-Metal Complexes Containing σ-Bonded, Unsaturated Hydrocarbon Ligands[1]

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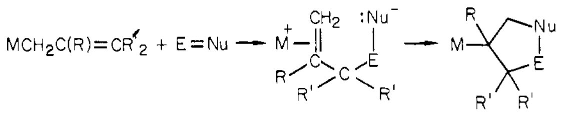
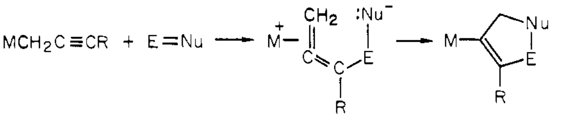
Several new transition-metal–cyclopentenyl and –cyclopentyl complexes were prepared by reactions of appropriate propargyl, allenyl, and η^1-allyl complexes of $\eta^5\text{-}C_5H_5Fe(CO)_2$, $Mn(CO)_5$, and $Re(CO)_5$ with *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$). Each cycloaddition reaction affords a mixture of diastereomers, some of which were separated. The ratio of diastereomers was determined by ^{19}F NMR spectroscopy, and the data were used to calculate percent stereoselectivities of these cycloadditions. The reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with *trans*-$C_6F_6N_2$ in benzene at room temperature proceeds with ca. 75% stereoselectivity whereas that of $M(CO)_5CH_2C{\equiv}CC_6H_5$ (M = Mn or Re) with *trans*-$C_6F_6N_2$ in benzene and acetonitrile, also at ca. 25 °C, occurs with a lower, 32–40%, stereoselectivity. Similar reactions with *cis*-$C_6F_6N_2$ appear to proceed substantially, if not completely, via *cis*-$C_6F_6N_2$ to *trans*-$C_6F_6N_2$ isomerization to give comparable stereoselectivities. The cycloadditions of the metal–allenyl and –η^1-allyl complexes did not furnish any reliable or readily interpretable stereochemical data. The results obtained herein rule out the possibility of a concerted mechanism for the reaction of transition-metal–propargyl complexes with $C_6F_6N_2$ and are consistent with the previously proposed two-step pathway.

Introduction

The addition of electrophilic reagents, E=Nu (E = electrophilic part, Nu = nucleophilic part), to η^1-allyl, propargyl, and allenyl ligands coordinated to transition metals has received considerable attention.[2,3] The reactions of the propargyl and allenyl fragments yield five-membered rings by (3 + 2) cycloaddition accompanied by 1,2 metal migration, whereas the reactions of the η^1-allyl moieties usually afford either analogous cycloadducts or insertion products. Support has been demonstrated[3-5] for similar, two-step paths (eq 1–3) of such cycloadditions.



(1)



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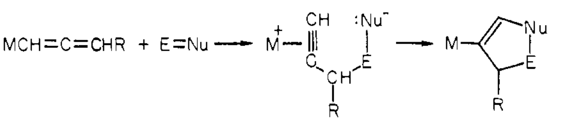


(3)

Only in reaction 1 has there been any direct evidence for the proposed path: when E=Nu is SO_2, a dipolar metal–η^2-olefin species has been recently detected and intercepted.[3,4] Reaction 2 has been simulated by protonation and treatment of the resultant cationic η^2-allene derivatives with nucleophiles to give iron–vinyl complexes.[5,6]

To elucidate further the mechanism of these reactions we undertook an investigation of stereochemistry at the E–Nu bond of the formation of the cycloadducts. For that purpose an ideal electrophile is an isomeric olefin for which a physical measurement can differentiate the stereochemistry of the reactant as well as that of the product. Such stereochemical investigations have been conducted by ^{19}F NMR spectroscopy for several cycloaddition reactions of 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$),[7-9] whose reactivity was shown to be similar to that of tetracyanoethylene (TCNE).

In this paper are reported the details of our study of the cycloaddition reactions of *cis*- and *trans*-$C_6F_6N_2$ with transition-metal–η^1-allyl, –propargyl, and –allenyl complexes conducted with a view to determining the stereoselectivity of these processes. Part of our work has been described in a preliminary communication.[10]

Results and Discussion

Characterization and Properties of Metal–Cyclopentenyl Complexes. Transition-metal–propargyl complexes react with $C_6F_6N_2$ at room temperature to yield 1:1 adducts as indicated by elemental analyses and mass spectrometry. These products

Table I. Infrared, ^{1}H NMR, and ^{19}F NMR Spectra of Cycloaddition Complexes

	Infrared, cm^{-1}		^{1}H NMR, τ[c]					
Complex	ν_{CO}[a]	ν_{CN}[b]	C_5H_5	CH_2	R	R′	C_6H_5	^{19}F NMR, ϕ[d]
IA	*f*	*f*	5.34 s	6.62, 6.72 AB (17)			2.64 br	67.67 q, 68.26 q (9.8)
IIA	2033 s, 1983 s	2254 w	5.34 s	6.53 s			2.64 br	68.62 s, 71.06 d[h]
IB	2058 m, 2033 s, 2018 sh	*f*		6.44, 6.64 AB (16.5)			2.61 br	67.15 q, 68.11 q (11)
IIB	2058 s, 2036 s	2256 w		6.42 s			2.58 br	68.56 s, 71.37 s
IC-IIC	2059 sh, 2030 s, 2011 m	2256 w		6.38 s, 6.49 br			2.53 br	67.13 q, 68.25 q (11), 68.55 s, 71.41 s
VIA	2037 s, 1988 s	*f*			*g*			68.22 q, 70.55 q (10.3), 71.82 s, 72.11 s
VIB	2031 s, 1981 s	*f*	5.1 br	6.5 s, 8.5 br				66.23 s, br, 73.14 s, br
VIIIA or IXA[e]	*f*	*f*			*f*			67.75 s
IXA or VIIIA[e]	*f*	*f*			*f*			67.46 s
XA	2016 s, 1962 s	2250 w	5.12 s		7.5 m, br			68.33 q, 69.09 q (2.8)
VIIIB or IXB[e]	2016 s, 1962 s	*f*	5.14 s	7.13 s	8.22 s	7.13 s		67.08 s
XB	2014 s, 1960 s	2250 w	5.13 s	7.06 s	8.37 s	7.11 s		68 m[i]
XC or XI[e]	2016 s, 1962 s	2254 w	5.12 s	7.30 s	7.35 s	8.51 s, 8.81 q (2)		61.58 m,[j] 69.48 q (5.2)
XI or XC[e]	*f*	*f*			*f*			62.33 m,[i] 68.60 q (2.9)

[a] CH_2Cl_2 solution. Abbreviations: s, strong; m, medium; sh, shoulder. [b] KBr pellet; w = weak. [c] $CDCl_3$ solution. All signals integrate for the proper number of protons; J_{H-H} (Hz) in parentheses. Abbreviations: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad. [d] Relative to $CFCl_3$, $\phi = 0.00$ ppm; $\phi(CFCl_3) = \phi(C_6H_5CF_3) + 63.75$ ppm; each pair of singlets and of 1:3:3:1 quartets is of equal intensity; J_{F-F} (Hz) in parentheses. [e] Structural assignment uncertain; see text. [f] Not recorded. [g] Not assigned: τ (area) 4.7 (1.3), 4.95 (2.0), 5.08, 5.11 (3.9), 6.5 (0.6), 6.7 (1.4), 8.1 (0.5). [h] $J_{H-F} = 1.4$ Hz. [i] Coupling not resolved. [j] $J_{H-F} = 2.5$ Hz.

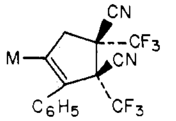
Table II. Carbon-13 NMR Spectra of $M\overline{C=C(R)ENuC}H_2$

Chemical shift (δ)[a] of complex								
IIA[b]	IIB[c,d]	IIIA[c]	IIIB[c]	IIIC[c,e]	IVA[b,f]	IVB[b,f]	V[b,f]	Assignment
213.45 212.68	208.37	213.55	214.3	208.24	218.56	213.57	212.67	M–CO
							163.10	C=O
160.21	166.38	164.4	156.2	164.17	148.65	153.71	186.59	$M-\overset{\vert}{C}=$
135.54	134.33	135.48	128.0	133.62	135.67	133.48	146.46	=C<
136.37	136.28	134.05		134.14	136.29	136.57	135.59	4° C of C_6H_5
131.58 128.33	131.54 128.87	130.74 129.24		130.89 129.20	131.06 127.80	131.51 127.80	130.22 128.42	} *o,m*-C_6H_5
128.55	129.28	129.4		129.85	127.80	127.58	128.03	*p*-C_6H_5
123.19 (285) 122.71 (287)	*g*				122.66 (287)	122.77 (288)		CF_3
113.52 112.20	113.27 112.19	112.74 111.4	112.8 111.2	112.17 110.61				CN
85.45		86.73	86.5		99.28	85.09	86.01	C_5H_5
56.54	54.44	57.61	57.4	56.65	89.58	89.47	64.91	CH_2
53.32 (29) *i*	52.8 (27) *h*	55.01 45.54	54.2 44.5	55.48 44.82	*h*	*h*		$-\overset{\vert}{\underset{\vert}{C}}-$
			15.5					CH_3

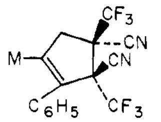
[a] Relative to TMS; J_{C-F} (Hz) in parentheses. [b] $CDCl_3$ used as solvent and lock. [c] $(CD_3)_2CO$ used as solvent and lock; $\delta(TMS) = \delta((CD_3)_2CO) + 29.22$ ppm. [d] Recorded at 195 K. [e] Recorded at 199 K. [f] Samples provided by Dr. D. W. Lichtenberg. [g] $^{13}C\{^{19}F\}$ NMR recorded at room temperature: δ 124, 123.28. [h] Not observed. [i] Possible quartet at δ 62.5 (30).

are air-stable, yellow (Fe) or white (Mn and Re) solids, the last two subliming at 70 °C (ca. 0.1 Torr). They are only slightly soluble in pentane but increasingly soluble in benzene, dichloromethane, and acetone.

By analogy with known cycloadducts derived from these propargyl complexes and various electrophiles,[2,3] the isolated products are expected to contain a cyclopentenyl ring σ bonded to the metal. Two diastereomerically related pairs of enantiomeric configurations are possible for the newly formed ring in these derivatives, those of I and II. These pairs were separated either partially or completely for M = η^5-$C_5H_5Fe(CO)_2$ and $Mn(CO)_5$ by a combination of chromatography and fractional crystallization.



IA, M = η^5-$C_5H_5Fe(CO)_2$
B, M = $Mn(CO)_5$
C, M = $Re(CO)_5$



IIA, M = η^5-$C_5H_5Fe(CO)_2$
B, M = $Mn(CO)_5$
C, M = $Re(CO)_5$

The gross features of the proposed cyclopentenyl ring structure are confirmed by the infrared, ^{1}H NMR, and ^{13}C NMR spectroscopic properties of the adducts, presented in Tables I and II. The infrared carbonyl stretching frequencies match well those reported for analogous cycloaddition products with various electrophiles.[5,11-15] The ^{1}H NMR spectra of these and other (3 + 2) cycloadducts are also quite similar. For example, the chemical shifts of the methylene protons of I and II fall in the range τ 6.38–6.66 compared to the values τ 6.30 and 6.41 for the TCNE adducts of the same propargyl complexes of manganese[16] (IIIC) and iron[17] (IIIA), respectively.

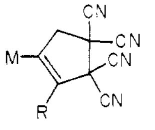
However the single most definitive evidence for the proposed gross structures of these products is provided by ^{13}C NMR spectroscopy. Table II contains the chemical shift data for

Table III. Carbon-13 NMR Spectra of Iron–Cyclopentyl Complexes

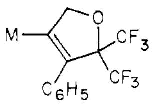
Chemical shift (δ)[a] of complex					Assignment
XA[c]	XB[c]	XC or XI[b,c]	VIIA[d]	VIIB[d]	
215.25	216.04 215.93	216.77 215.76	216.67	217.2 216.3	CO
123.14 (285) 122.35 (285)	122.91 (285) 122.58 (285)	123.5 (285) 122.6 (289)			CF_3
113.98 113.30	114.15 113.64	114.3 113.5	113.77 113.06	114.09 111.82	CN
85.54	86.33	86.21	87.25	87.18	C_5H_5
50.92	57.88	57.38		60.01	CR'_2
			61.38		
49.96	56.20	49.29		53.19	CH_2
55.9 (30) 53.8 (30)	56.20 (30) 53.53 (30)	~52	45.32	56.3 43.9	CN \ / *C* / \
12.48	30.74	29.17	33.68	*e*	Fe–C
	39.23	26.70 22.40 (4)	37.20	26.14 23.30	CH_3

[a] Relative to TMS; J_{C-F} (Hz) in parentheses. [b] Structural assignment uncertain; see text. [c] $CDCl_3$ used as solvent and lock. [d] $(CD_3)_2CO$ used as solvent and lock; $\delta(TMS) = \delta((CD_3)_2CO) + 29.22$ ppm. [e] Obscured by $(CD_3)_2CO$.

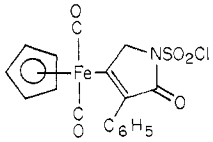
II. As yet unreported ^{13}C NMR spectra of the known, related (3 + 2) cycloaddition complexes III–V are included for



IIIA, M = η^5-$C_5H_5Fe(CO)_2$, $R = C_6H_5$
B, M = η^5-$C_5H_5Fe(CO)_2$, $R = CH_3$
C, M = $Mn(CO)_5$, $R = C_6H_5$



IVA, M = η^5-$C_5H_5Mo(CO)_3$
B, M = η^5-$C_5H_5Fe(CO)_2$



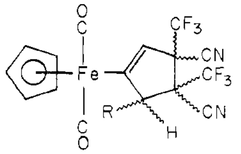
V

comparison. Several chemical shift assignments were verified by single-frequency off-resonance decoupled (SFORD) spectra. It is to be noted that the position of the various resonances of II matches closely that of the corresponding signals of the TCNE and $CF_3C(O)CF_3$ cycloadducts, III and IV, respectively. The nonequivalence of the carbonyl carbons, observed for IIA, was reported previously for another η^5-$C_5H_5Fe(CO)_2R$ complex with an asymmetric alkyl ligand R, that with R = $CH(CH_3)C_6H_5$.[18]

The diastereomerically related pairs of enantiomers (henceforth called diastereomers) I and II differ in the relative positions of the CN and CF_3 groups on adjacent carbons: in I the two like substituents are cis whereas in II they are trans. These relative orientations are most readily discerned by ^{19}F NMR spectroscopy as demonstrated earlier for similar organic cycloadducts by Proskow, Simmons, and Cairns.[7] The spectra of I and II, listed in Table I, show two ^{19}F resonances for the nonequivalent CF_3 groups in both I and II. However, the $J_{CF_3-CF_3}$ values for nonequivalent cis CF_3 groups are much larger (10–11 Hz) than those for nonequivalent trans CF_3 groups, which appear to be zero, owing to through-space F–F coupling.[19] Thus the spectra of I consist of two 1:3:3:1 equal-intensity quartets whereas the spectra of II are comprised of two equal-height singlets, readily distinguishing these diastereomers. Moreover, in all cases the chemical shifts of II occur at higher fields than those of I.

The only additional substantial spectroscopic difference between the diastereomers I and II occurs in the methylene region of the ^1H NMR spectra. Whereas the diastereomers I exhibit an AB pattern with $J_{H_A-H_B} = 16$–17 Hz, as expected for magnetically nonequivalent geminal protons, the diastereomers II show the corresponding resonance as a singlet. This observation may be compared to those made on other (3 + 2) cycloaddition complexes with chiral centers: the SO_2 adducts[13a] exhibit magnetic nonequivalence of the CH_2 protons but the $ClSO_2NCO$ adducts[15a] and some $(t$-$C_4H_9)(CN)$-$C{=}C{=}O$ adducts[20] do not. The methylene protons occur at slightly higher fields in I relative to II.

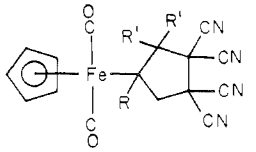
Preliminary results show that the reaction of η^5-$C_5H_5Fe(CO)_2CH{=}C{=}CHR$ with *trans*-$C_6F_6N_2$ affords 1:1 adducts as indicated by mass spectrometry. When R = H, two apparently isomeric solids were isolated in low yield after chromatography. The first solid was obtained in insufficient amount for satisfactory characterization, and the second solid appears from spectroscopic data (Table I) to be a mixture of the two possible diastereomers of VIA. When R = CH_3, the product could not be satisfactorily purified, but its spectra (Table I) indicate the predominance of one of the possible four diastereomers of VIB, with the CN groups trans to the CF_3 groups.



VIA, R = H
B, R = CH_3

Characterization and Properties of Metal–Cyclopentyl Complexes. Both *cis*- and *trans*-$C_6F_6N_2$ react with several iron–η^1-allyl complexes to yield 1:1 adducts based on elemental analyses and mass spectrometry. These air-stable, yellow compounds exhibit solubility properties similar to those of the iron–cyclopentenyl derivatives.

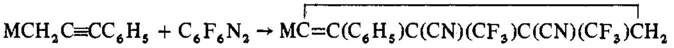
The infrared, ^1H NMR, and ^{13}C NMR spectroscopic properties, entered in Tables I and III, support the gross features of the proposed iron–cyclopentyl structures of these complexes. The carbonyl stretching frequencies and the chemical shifts in the ^1H NMR spectra match well the corresponding data reported for other, similar (3 + 2) cycloadducts.[2,3,11–15] Again, however, the most definitive evidence for the assigned ring structures is provided by ^{13}C NMR spectroscopy. Comparison of the spectra of these $C_6F_6N_2$ adducts with those of analogous TCNE adducts, VII, included in Table III, reveals close similarity in the chemical shift of the corresponding carbon atoms. The observed agreement is structurally significant as one of the TCNE-derived complexes included for comparison, VIIA, was recently characterized crystallographically.[21]



VIIA, R = CH_3, R' = H
B, R = H, R' = CH_3

The new cyclopentyl complexes can exist in several diastereomeric forms the number of which depends on the nature of the substituent R′. Thus for the more symmetrical molecules (R = H and CH_3; R′ = H), two meso isomers with cis

Table IV. Stereochemical Data for the Reaction

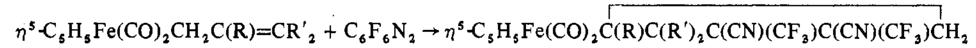


$$MCH_2C{\equiv}CC_6H_5 + C_6F_6N_2 \rightarrow MC{=}C(C_6H_5)C(CN)(CF_3)C(CN)(CF_3)CH_2$$

M	$C_6F_6N_2$	mol of M-C_9H_7/mol of $C_6F_6N_2$	Solvent	Reacn time, h	%: Yield product	%: Recovered M-C_9H_7	% diastereomer[a]: I	% diastereomer[a]: II	% stereo-selectivity
η^5-$C_5H_5Fe(CO)_2$	Trans	1.03	C_6H_6	0.08	54	5	9	91	82
	Trans	0.42	C_6H_6	0.75	*b*	*b*	16	84	68
	Cis	0.46	C_6H_6	1.25	*b*	*b*	7	93	86
	Cis	1.0	CH_3CN	0.25	*b*	*b*	9	91	82
$Mn(CO)_5$	Trans	1.0	C_6H_6	44	48	39	34	66	32
	Trans	1.0	CH_3CN	5.5	90	0	30	70	40
	Cis	1.0	C_6H_6	68	53	39	43	57	14
$Re(CO)_5$	Trans	*b*	CH_3CN	0.08	*b*	0	30	70	40

[a] Values reproducible to within ±3% in duplicate runs under similar conditions. [b] Not calculated.

Table V. Stereochemical Data for the Reaction

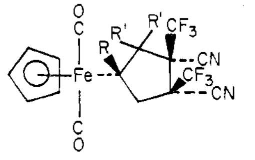


$$\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(R){=}CR'_2 + C_6F_6N_2 \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2C(R)C(R')_2C(CN)(CF_3)C(CN)(CF_3)CH_2$$

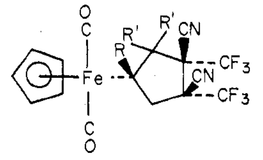
R	R'	$C_6F_6N_2$	mol of Fe allyl/mol of $C_6F_6N_2$	Solvent	Reacn time, h	% yield	% diastereomer: Cis 1	% diastereomer: Cis 2	% diastereomer: Trans 1	% diastereomer: Trans 2	% stereo-selectivity, trans 1,2
H	H	Trans	1.33	C_6H_6	0.5	94	2.0	0.8	97.2		94
CH_3	H	Trans	1.24	C_6H_6	0.1	79	1.7	*a*	98.3		97
		Cis	1.41	C_6H_6	0.1	92	27	*a*	73		46
		Cis	1.11	CH_3CN	0.1	89	9	*a*	91		82
H	CH_3	Trans	1.0	C_6H_6	71	*b*	*a*	*a*	*b*	*b*	*b*
		Trans	1.9	CH_3CN	13.5	*b*	*a*	*a*	81	12[c]	100
		Tans	1.0	CH_3CN	0.8	*b*	*a*	*a*	84	16	100

[a] Not observed. [b] Not calculated. [c] The remaining percent consists of an uncharacterized product; see also Table VI, footnote *g*.

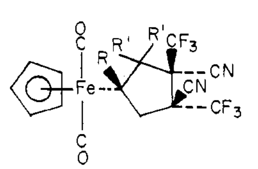
CF_3 groups and one pair of enantiomers with trans CF_3 groups are possible. These three diastereomers are depicted in VIIIA–XA and VIIIB–XB. Only in XA and XB are the CF_3 substituents nonequivalent. For the cycloaddition product with R = H and R' = CH_3, four diastereomers (each a pair of enantiomers), VIIIC–XC and XI, can be formed, and all four have nonequivalent CF_3 groups. Fluorine-19 NMR spectroscopy distinguishes some of these configurations.



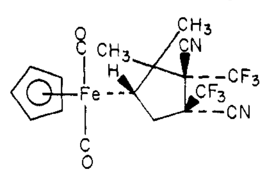
VIIIA, R = R' = H
B, R = CH_3, R' = H
C, R = H, R' = CH_3



IXA, R = R' = H
B, R = CH_3, R' = H
C, R = H, R' = CH_3



XA, R = R' = H
B, R = CH_3, R' = H
C, R = H, R' = CH_3



XI

The ^{19}F NMR spectrum of the cyclopentyl product mixture with R = R' = H shows two small singlets of different intensity and a 1:3:3:1 quartet and a multiplet of equal intensity. The two singlets are assigned to the equivalent CF_3 groups of VIIIA and IXA but the correspondence between the signals and the diastereomers cannot be ascertained. The other resonances are ascribed to XA. Separation of these diastereomers was successful enough to demonstrate the existence of three different complexes as detailed in the Experimental Section. The $^{19}F\{^1H\}$ NMR spectrum of XA collapsed the multiplet into a 1:3:3:1 quartet, indicating that one of the nonequivalent CF_3 groups was proton-coupled. The coupled hydrogen may be that on the carbon bonded to the metal. Similar long-range H–F coupling has been reported in the literature.[22] The coupling constant $^5J_{CF_3\text{-}CF_3(\text{trans})}$ = 2.8 Hz for XA may be compared with the reported[9] $^5J_{CF_3\text{-}CF_3(\text{trans})}$ = 4–6 Hz for some bicyclic [4.2.1] derivatives of iron obtained from $C_6F_6N_2$ and coordinated cycloheptatrienes.

Only two diastereomers were observed in the ^{19}F NMR spectra of the cycloadducts with R = CH_3 and R' = H and with R = H and R' = CH_3. When R = CH_3 and R' = H, XB and either VIIIB or IXB were detected and subsequently separated chromatographically. When R = H and R' = CH_3, only the two trans diastereomers, XC and XI, were observed, in unequal amounts. They were successfully separated by column chromatography. Thus it appears that the undetected cis diastereomers for the cycloadducts with R = CH_3 and R' = H and with R = H and R' = CH_3 are at best formed in insufficient quantities to be spectroscopically observable. Steric factors associated with the presence of the substituent methyl groups may be involved in this selectivity when R = H and R' = CH_3.

Stereoselectivity of Cycloaddition Reactions. Stereochemical data for the cycloadditions in point were obtained by allowing the metal complexes to react with *cis*- or *trans*-$C_6F_6N_2$ in benzene or acetonitrile at room temperature for various lengths of time. The ratio of the diastereomeric products was then determined by the integration of the appropriate resonances in the ^{19}F NMR spectrum of the reaction mixture. These data are listed in Tables IV and V.

The isomer *trans*-$C_6F_6N_2$ reacts with η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ to form predominantly, with ca. 75% stereoselectivity, the cyclopentenyl complex in which the CF_3 groups are trans, IIA. Likewise, *trans*-$C_6F_6N_2$ undergoes cycloaddition reaction with each of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$

and $Re(CO)_5CH_2C{\equiv}CC_6H_5$ to afford mainly the cyclopentenyl complexes with trans CF_3 groups, IIB and IIC, respectively, but with lower stereoselectivities of ca. 32–40%.

The isomer *cis*-$C_6F_6N_2$ reacts more slowly than *trans*-$C_6F_6N_2$ with the iron and manganese propargyls to yield predominantly IIA and IIB, with stereoselectivities similar to those given above. It was further noted that the thermodynamically less stable *cis*-$C_6F_6N_2$[7] isomerizes to *trans*-$C_6F_6N_2$ in the course of its reaction with $Mn(CO)_5CH_2C{\equiv}CC_6H_5$. These observations suggest that the similar stereoselectivities of the corresponding cycloadditions of *trans*- and *cis*-$C_6F_6N_2$ are likely the result of the predominant, if not exclusive, reaction of *trans*-$C_6F_6N_2$ with the propargyl ligand in both cases.

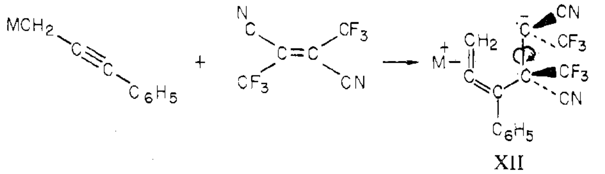
An equilibrium mixture of $C_6F_6N_2$ is reported[7] to contain a trans:cis ratio of greater than 95:5. Since *cis*-$C_6F_6N_2$ isomerizes to *trans*-$C_6F_6N_2$ during the reactions studied, conversely some *cis*-$C_6F_6N_2$ is expected when one starts with *trans*-$C_6F_6N_2$. Although no *cis*-$C_6F_6N_2$ was observed by VPC, its presence in the reaction mixtures cannot be precluded. Notwithstanding this, one can rule out the possibility that all of the observed I results from direct reaction of *cis*-$C_6F_6N_2$ formed via isomerization of the starting *trans*-$C_6F_6N_2$. As noted in Table IV, *cis*-$C_6F_6N_2$ reacts with the propargyl moiety more slowly than does *trans*-$C_6F_6N_2$. Even if the cis–trans equilibrium were rapidly established in reactions of *trans*-$C_6F_6N_2$—and this does not occur for *cis*-$C_6F_6N_2$—a 100% stereospecific reaction of all the *cis*-$C_6F_6N_2$ available would limit the amount of I formed to less than 5%.

It was further ascertained that there is no epimerization of the products subsequent to the reaction. The cycloadducts were found to display configurational stability toward prolonged storage in chloroform or benzene solution with or without added excess $C_6F_6N_2$ and toward chromatography on alumina. Thus the observed loss in stereochemistry about the carbon–carbon bond in the reaction of *trans*-$C_6F_6N_2$ with metal–propargyl complexes must take place during the cycloaddition itself.

The products from reaction of *trans*-$C_6F_6N_2$ with the iron–allenyl complexes were not characterized as unequivocally as I and II. However, the ^{19}F NMR spectrum of VIA indicates that a mixture was formed of the cyclopentenyl diastereomers with the CF_3 groups both cis and trans. By arguments similar to those invoked for the cycloaddition of metal–propargyl complexes, a loss in stereochemistry may be occurring during the reaction.

The reactions of the iron–η^1-allyl complexes with *trans*-$C_6F_6N_2$ afford only very small amounts of the cyclopentyl diastereomers with cis CF_3 groups. Thus one cannot conclude unequivocally whether these diastereomers arise during the reaction itself or result from prior isomerization of *trans*-$C_6F_6N_2$.

Since it has been shown that the formation of metal–cyclopentenyl derivatives with cis CF_3 groups, I, from *trans*-$C_6F_6N_2$ and metal–propargyl complexes occurs during the reaction itself, the observed loss in stereochemistry requires that the cycloaddition be nonconcerted. Thus these data are consistent with the two-step mechanism in eq 4, which is



XII

—→ I + II (4)

strictly analogous to the general mechanism presented in eq 2. The loss in stereochemistry would result from rotation of 180° about the indicated carbon–carbon bond and rapid inversion of configuration at the carbanion carbon in the dipolar intermediate XII. The appreciable enhancement of the rate of reaction between $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ and *trans*-$C_6F_6N_2$ on going from benzene to the more polar acetonitrile solvent is in accord with such a two-step mechanism.

In conclusion, the possibility of a concerted mechanism for the reaction of metal–propargyl compounds with $C_6F_6N_2$ has been ruled out; the results are in agreement with the proposal that coordinated η^1-allyl and propargyl ligands undergo cycloaddition through strictly analogous pathways.

Experimental Section

Analyses and Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken in evacuated tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Vapor-phase chromatography (VPC) was carried out on a Varian Associates Aerograph Autoprep Model 700 instrument using a 25 ft × $^3/_8$ in. column packed with 15% QF-1 on Chrom W treated with a methylsilylating agent.

Hydrogen-1 NMR spectra were recorded on Varian Associates A-60A and HA-100 spectrometers using tetramethylsilane (TMS) as an internal reference. Fluorine-19 NMR spectra were measured on a Varian Associates HA-100 spectrometer at 94.1 MHz using $C_6H_5CF_3$ as the solvent and lock, or on a Bruker HX-90 spectrometer at 84.6 MHz using $CDCl_3$ as the solvent and lock and $C_6H_5CF_3$ as an internal reference. Carbon-13 NMR spectra were recorded on the Bruker HX-90 at 22.625 MHz in a Fourier transform mode. All spectra recorded on the Bruker HX-90 were obtained with the assistance of Dr. C. E. Cottrell and Mr. J. M. Geckle.

Tabulated infrared ν_{CO} and ν_{CN} values were obtained using a Beckman IR-9 spectrophotometer; routine infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Mass spectra were obtained at 70 eV on an AEI Model MS-9 spectrometer by Mr. C. R. Weisenberger.

Materials. 1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$) was prepared by the literature method[7] using an alternative procedure for the synthesis of the precursor trifluoroacetaldehyde cyanohydrin.[23] The isomers were separated by VPC at 75 °C.

Tetrahydrofuran (THF) and pentane were distilled under nitrogen from $LiAlH_4$ and CaH_2, respectively, prior to use. Other commercially procured chemicals and solvents were reagent grade quality and were used without further purification.

Reactions were carried out under a slight positive pressure of dry nitrogen and solvents were saturated with nitrogen before use.

The compounds η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'_2$ (R = R′ = H;[24] R = CH_3, R′ = H;[11] R = H, R′ = CH_3[25]), $MCH_2C{\equiv}CC_6H_5$ (M = η^5-$C_5H_5Fe(CO)_2$,[26] $Mn(CO)_5$[12]), and η^5-$C_5H_5Fe(CO)_2CH{=}C{=}CHR$ (R = H, CH_3[26,27]) were prepared by known literature procedures. The hitherto unreported $Re(CO)_5CH_2C{\equiv}CC_6H_5$ was synthesized by an analogous method. A THF solution (50 mL) of $NaRe(CO)_5$ from 2.00 g (3.07 mmol) of $Re_2(CO)_{10}$ and 0.180 g (7.82 mmol) of Na in 100 mL of Hg was slowly added to a stirred solution of $C_6H_5C{\equiv}CCH_2Cl$ (1.11g, 7.29 mmol) in 20 mL of THF at 0 °C. The resulting solution was allowed to warm to room temperature overnight. Removal of the solvent and chromatography on alumina (neutral, 6% H_2O) using pentane eluent first yielded $Re_2(CO)_{10}$ and then a mixture of $Re(CO)_5CH_2C{\equiv}CC_6H_5$ and $C_6H_5C{\equiv}CCH_2Cl$. The latter effluent was concentrated to an oil (1.7 g) and cooled to −78 °C to give off-white crystals of $Re(CO)_5CH_2C{\equiv}CC_6H_5$ which were collected and washed with cold pentane; yield ca. 25 mg, mp 56–58 °C. The solid is stable under nitrogen at −15 °C but turns to an oil in air at 25 °C: IR ν_{CO}(pentane) 2065 (sh), 2033 (vs), and 1990 (m) cm^{-1}; ^1H NMR ($CDCl_3$) τ 2.67 br and 8.33 s. The mass spectrum (source temperature 45 °C) shows a peak at *m/e* 442 of the parent ion $^{187}Re(CO)_5C_9H_7^+$.

Preparation of Cycloaddition Complexes. A typical synthesis is described for η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and *trans*-$C_6F_6N_2$. Details of the preparation of other cycloaddition products, as well as analytical data and physical properties, are furnished in Tables IV–VI.

The isomer *trans*-$C_6F_6N_2$ (0.450 g, 2.10 mmol) in 25 mL of benzene was added to a stirred benzene solution (25 mL) of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.634 g, 2.17 mmol) under nitrogen. The

Table VI. Analytical Data and Physical Properties of Cycloaddition Complexes

			Analyses, %					
			C		H		Mol wt	
Complex	Mp, °C	Color	Calcd	Found	Calcd	Found	Calcd[a]	Found[b]
IIA	144.7–145.3	Yellow	52.17	52.30	2.37	2.41	506	506
IB	121.5–122.5	White	45.80	46.01	1.34	1.39	524	524
IIB	124–124.5	White						
IC–IIC[c]	103.5–105.5	White	36.62	36.85	1.07	1.21	654	654
VIA[d,e]	94–96	Tan			h		430	430
VIB[f]	Oil	Brown			h		444	444
XA	115–115.7	Yellow	44.44	44.31	2.31	2.44	432	432
VIIIB or IXB	149–150	Yellow						
XB	139–139.5	Yellow	45.74	45.83	2.69	2.70	446	446
XC or XI[g]	113–113.7	Yellow	46.96	47.14	3.04	3.09	460	460

[a] Calculated for the most common isotopic species. [b] Parent ion in the mass spectrum at 70 eV. [c] Mixture of diastereomers. [d] Reaction time 1.5 h; *trans*-$C_6F_6N_2$. [e] Another, brown isomer (*m/e* 430) separated by chromatography; mp 72–76 °C; ν_{CO} 2032, 1983 cm^{-1}. [f] Reaction time 0.1 h; *trans*-$C_6F_6N_2$. [g] Major trans diastereomer. Uncharacterized mixture also obtained: ν_{CO} 2016, 1962 cm^{-1}; ^1H NMR (τ) 5.12, 6.8–8.2, 8.61, 8.72, 8.84, 8.92, 8.96; ^{19}F NMR (ϕ) 69.98 s, 73.09 s, 75.11 s of different intensity. [h] Compound not analytically pure.

reaction appeared complete in 5 min as inferred by infrared spectroscopy. The solvent was then removed and the residue was introduced onto a 2 × 12 cm column of alumina (neutral, 10% H_2O) with a minimum of benzene. Elution with pentane developed a yellow band which yielded unreacted η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.030 g, 0.010 mmol) upon removal of the solvent, whereas elution with 1:1 pentane–benzene developed a broad yellow band. Removal of the solvent afforded 0.577 g (54% yield) of yellow 1:1 cycloaddition product.

The reaction mixtures containing $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ and $C_6F_6N_2$ were examined periodically by VPC. *trans*-$C_6F_6N_2$ showed no evidence of isomerization in these experiments; however, *cis*-$C_6F_6N_2$ did isomerize gradually as the reaction progressed (e.g., a ca. 1:1 mixture of isomers was detected after 20 h in benzene solution).

Separation of Diastereomers. (a) Metal–Cyclopentenyl Complexes. This was accomplished by a combination of column chromatography and fractional crystallization from benzene–pentane.

The more abundant isomers IIA and IIB were obtained by chromatography of the respective reaction mixtures on a 2 × 14 cm column of alumina (neutral, 6% H_2O) using 2:1 pentane–benzene eluent. Collection of ca. half of the resulting broad band and fractional crystallization of the solid content from pentane–benzene afforded pure IIA and IIB as the less soluble isomers.

Pure IB was obtained by combining the last one-fourth of the band from two separate chromatographies as above and rechromatographing their contents. The trailing one-fourth of the eluted band contained 97:3 IB:IIB. Fractional crystallization of this sample from pentane–dichloromethane yielded pure IB.

Because of the low yield of IA in every reaction, only a partial separation of IA from IIA was achieved. The trailing half of the chromatographic band from IA–IIA was collected and the material was rechromatographed. The back one-fourth of the band was collected and set aside whereas the remaining portion was rechromatographed again. This last procedure was repeated twice, all three back fractions were combined, and the resultant material was fractionally crystallized from 2:1 pentane–benzene. Removal of the solvent from the filtrate yielded ca. 90:10 IA:IIA.

The diastereomers VIA were separated from another, minor isomer by chromatography of the reaction mixture on a 2 × 14 cm column of alumina (neutral, 6% H_2O). Elution with pentane–benzene yielded the minor isomer whereas elution with benzene afforded VIA.

The product VIB could not be separated into the expected isomers either by chromatography on alumina (neutral, 6% H_2O) or by crystallization from 2:1 pentane–benzene and 4:1 pentane–dichloromethane.

(b) Metal–Cyclopentyl Complexes. In a typical separation ca. 0.57 g of the cycloadduct from the reaction of *trans*-$C_6F_6N_2$ with η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ was introduced onto a 2.2 × 14 cm column of Florisil and eluted with 5:2 pentane–dichloromethane to give a broad yellow band. Most of this band was collected and solvent was removed to give yellow crystals of XA (ca. 0.50 g). The remaining portion of the band was similarly rechromatographed and yielded two slightly separated bands. The first was identified to contain XA whereas the second consisted of 69% VIIIA, 6% IXA, and 25% XA. Fractional crystallization from pentane–benzene resulted in the isolation of a small amount of yellow crystals shown to be a mixture of VIIIA (82%) and XA (18%).

Stability of Metal–Cyclopentenyl Complexes. Although a small amount of decomposition material was sometimes observed upon chromatography of reaction mixtures, no other metal carbonyl species were ever detected. Elution of a 22:78 mixture of IA–IIA on a 2 × 12 cm column of alumina (neutral, 6% H_2O) with 3:1 pentane–benzene for 2 h afforded the same 22:78 mixture. No change in the isomer ratio was observed after these complexes had been stored in $CDCl_3$ or C_6D_6 solution for 24 h.

Addition of a fourfold excess of *trans*-$C_6F_6N_2$ to a 94:6 mixture of IB–IIB in $CDCl_3$ and storage of the resultant solution for 5 days at 25 °C also did not alter the isomer ratio.

Determination of Ratio of Diastereomers in Mixtures. The ratio of the diastereomeric products was determined by integrating the appropriate resonances in the ^{19}F NMR spectrum of the reaction mixture. With the spectra recorded on the Varian HA-100, the average of four integrations was used to calculate the ratio of the isomers. With those recorded on the Bruker HX-90, calculation of the isomeric ratio was made from instrument-computed areas. The integrations were found to be reproducible to ±2%.

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Registry No. IA, 59247-17-5; IB, 59247-18-6; IC–IIC, 63730-29-0; IIA, 59218-80-3; IIB, 59218-81-4; IIIA, 63703-83-3; IIIB, 53261-31-7; IIIC, 63703-84-4; IVA, 54774-69-5; IVB, 54657-50-0; V, 40196-28-9; VIA, 63703-85-5; VIB, 63703-86-6; VIIA, 34676-40-9; VIIB, 53261-30-6; VIIIA, 63783-42-6; VIIIB or VB, 63703-80-0; IXA, 63703-81-1; XA, 63783-43-7; XB, 63730-27-8; XC, 63703-82-2; XI, 63730-28-9; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, 23626-46-2; $Re(CO)_5CH_2C{\equiv}CC_6H_5$, 59094-87-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$, 38960-10-0; η^5-$C_5H_5Fe(CO)_2CH_2CH(CH_3){=}CH_2$, 31781-60-9; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, 38905-70-3; $Re_2(CO)_{10}$, 14285-68-8; $C_6H_5C{\equiv}CCH_2Cl$, 3355-31-5; *trans*-$C_6F_6N_2$, 2167-31-9; *cis*-$C_6F_6N_2$, 2167-32-0; ^{13}C, 14762-74-4.

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Formation of Transient $(CH_3)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2Pb$ Species via Methylation of Zn^{2+}, Cd^{2+}, and Pb^{2+} by a *trans*-Dimethylcobalt Complex

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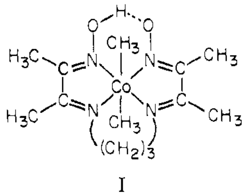
The methylation reactions in i-C_3H_7OH of Zn^{2+}, Cd^{2+}, and Pb^{2+} by an excess of the *trans*-dimethylcobalt complex, $(CH_3)_2Co(BDM1,3pn)$, are discussed. (BDM1,3pn is a mononegative, tetradentate dioxime diimine ligand formed by the condensation of 2 mol of 2,3-butanedione and 1 mol of 1,3-propanediamine.) With a 2:1 complex:metal ratio a very rapid reaction forms $CH_3Co(BDM1,3pn)^+$ and CH_3M^+ ($M^{2+} = Zn^{2+}$, Cd^{2+}, and Pb^{2+}). Then in a slower reaction CH_3M^+ reacts with a second mole of $(CH_3)_2Co(BDM1,3pn)$ to form unstable $(CH_3)_2M$ species. These compounds rapidly react yielding CH_4 and a variety of nonvolatile products such as $[CH_3Cd(i\text{-}C_3H_7O)]_4$. The progress of the reactions was followed by the absorbance decrease of $(CH_3)_2Co(BDM1,3pn)$ and a GC analysis of CH_4.

Introduction

Reactions in which alkyl groups are transferred from synthetic monoalkylcobalt complexes to metal electrophiles have been the subject of intensive investigations in recent years. Interest in these reactions has been heightened by the demonstrated microbiological methylation of mercury,[1] lead,[2,3] and selenium[4] in the aquatic environment. Studies on organocobalt complexes include alkyl transfer from $RCo^{III}(chel)$[5] and alkylcobalamins to Hg^{2+}, Cr^{2+}, and Tl^{3+}.[6-13] These reactions invariably exhibit a 1:1 stoichiometry and result in the products shown in eq 1.

$$RCo^{III}(chel) + Hg^{2+} \rightarrow Co^{III}(chel)^+ + RHg^+ \tag{1}$$

Despite the ready cleavage of the Co–C bond by Hg^{2+}, Cr^{2+}, and Tl^{3+} a surprising number of other electrophilic reagents including H_3O^+, CH_3Hg^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Al^{3+} are unreactive toward monoalkylcobalt chelates.[14] Consequently, we became interested in studying the reactions of the *trans*-dimethyl complex $(CH_3)_2Co(BDM1,3pn)$ (structure I)



I

with light[15] and selected metal electrophiles. This interest was heightened by earlier studies with monomethylcobalt complexes which established the superior σ-donor and trans-labilizing character of CH_3 relative to other Lewis bases.[16,17] Our thinking in this regard was that one methyl group would be extremely susceptible to electrophilic attack and that methyl-transfer reactions with previously unreactive electrophiles might be made to occur.

In a recent paper we described the results of a detailed study on the 1:1 reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} in i-C_3H_7OH.[18] We reported that I reacts nearly instantaneously with a stoichiometric amount of all three metal ions to give quantitative yields of the corresponding monomethylcobalt derivative, $CH_3Co(BDM1,3pn)^+$, and surprisingly stable organometallic products of the type CH_3M^+ (eq 2). These

$$(CH_3)_2Co(BDM1,3pn) + M^{2+} \xrightarrow{\text{fast}} CH_3Co(BDM1,3pn)^+ + CH_3M^+ \tag{2}$$

results are of particular interest since no reaction has been previously reported in which these metal ions bring about the cleavage of a Co–C bond in complexes of macrocyclic ligands. In the present work we will discuss the 2:1 (complex:metal) reactions of I with these same metal ions and present evidence for the formation of transient $(CH_3)_2Zn$, $(CH_3)_2Cd$, and $(CH_3)_2Pb$ species.

Results and Discussion

The anaerobic 2:1 (complex:metal) reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} in i-C_3H_7OH are markedly different from the 1:1 reaction of I with these same metal ions. Instead of a single instantaneous reaction (eq 2) a two-step reaction was observed in which an initial fast step was followed by a second slower reaction which was complete in a matter of minutes. The biphasic nature of this reaction was confirmed using the stopped-flow technique to follow the decrease in absorbance of I at 412 nm (ε 8380).

The presence of isosbestic points at 490 and 450 nm indicate that only one complex product was formed in solution. In