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Kinetic Study of Cycloaddition Reactions of Transition Metal-Propargyl and -η^1-Allyl Complexes with *p*-Toluenesulfonyl Isocyanate[1]

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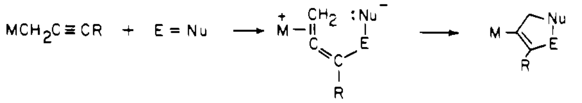
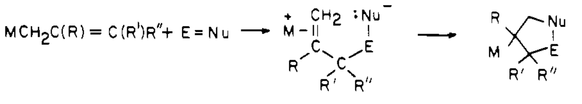
Reactions between transition metal-propargyl complexes ($MCH_2C{\equiv}CR$) and various unsaturated electrophiles have been examined with a view to finding a system that is readily amenable to a kinetic study under ambient conditions. The reaction between $MCH_2C{\equiv}CR$ and *p*-toluenesulfonyl isocyanate (TSI), which proceeds cleanly, with no observable intermediates, to the [3+2] cycloadducts $M\overline{C{=}C(R)C(O)N[S(O)_2C_6H_4CH_3\text{-}p]CH_2}$, was followed kinetically by infrared and, in some cases, ^1H NMR spectroscopy, mostly in CH_2Cl_2 at 25.0 °C. The cycloaddition is first order in each of $MCH_2C{\equiv}CR$ and TSI; for a given R, the bimolecular rate constants decrease as a function of M in the order $\eta^5\text{-}C_5H_5Cr(NO)_2 > \eta^5\text{-}C_5H_5Fe(CO)_2 > \eta^5\text{-}C_5H_5Mo(CO)_3 > \eta^5\text{-}C_5H_5W(CO)_3 > Mn(CO)_5$, spanning 2 orders of magnitude. Replacement of a CO in $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ or $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ with a better σ-bonding ligand (L) leads to an acceleration in the rate of the addition, which depends on ligand basicity, viz., $L = P(C_6H_5)_3 > P(OC_6H_5)_3 > CO$. Methylpropargyl complexes ($MCH_2C{\equiv}CCH_3$) react 16–30 times as rapidly as the corresponding phenylpropargyl complexes ($MCH_2C{\equiv}CC_6H_5$). Solvent influence on the rate of the reactions of $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with TSI in toluene, chlorobenzene, CH_2Cl_2, or CH_3CN is very small; the activation parameters for the first-mentioned reaction in toluene are $E_a = 11.5$ kcal/mol, $\Delta H^{\ddagger} = 10.9$ kcal/mol, and $\Delta S^{\ddagger} = -31$ eu. These data do not distinguish between a two-step dipolar mechanism and a concerted one, but the former is favored on the basis of the earlier stereochemical studies. The related reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(R){=}C(R')R''$ with TSI to give $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(R)C(R')(R'')C(O)N[S(O)_2C_6H_4CH_3\text{-}p]CH_2}$ was also investigated kinetically in CH_2Cl_2 at 25.0 °C; the bimolecular rate constants decrease as a function of the η^1-allyl ligand in the order $CH_2CH{=}CHCH_3 > CH_2CH{=}C(CH_3)_2 > CH_2CH{=}CH_2 \gtrsim CH_2CH{=}CHC_6H_5$, indicating that both steric and electronic effects are contributing. Surprisingly, structurally related $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}CHR''$ (R = R'') cycloadd TSI at comparable rates.

Introduction

The subject of the [3+2] cycloaddition reactions of transition metal-propargyl and -η^1-allyl complexes with various unsaturated electrophilic reagents, E=Nu (E = electrophilic part, Nu = nucleophilic part; eq 1 and 2), has received considerable attention in recent years.[2-6] These reactions are quite general for a number of molecules E=Nu, including $(NC)_2C{=}C(CN)_2$ (TCNE),[5,7] $(CF_3)_2CO$,[8] $ClS(O)_2NCO$,[5,9] and $RS(O)_2NSO$,[10] to mention a few. They appear to proceed in two steps, via a dipolar metal-η^2-allene or -η^2-olefin intermediate.[11,12]



(1)



(2)

Several aspects of the cycloaddition remain to be elucidated, however. Foremost among them is the effect of the metal and ancillary ligands on the relative reactivity toward a given E=Nu of the unsaturated hydrocarbon fragment in these complexes. This question has been addressed, but in a limited way, only for the η^1-allyl complexes. It was found that the relative reactivity of $MCH_2CH{=}CH_2$ toward $o\text{-}ClC_6H_4CH{=}C(CN)_2$ follows the order $M = \eta^5\text{-}C_5H_5Fe(CO)_2 > \eta^5\text{-}C_5H_5W(CO)_3 \gg \eta^5\text{-}C_5H_5Cr(NO)_2$.[5] More recently, the order $M = \eta^5\text{-}C_5H_5Fe(CO)[P(OCH_2)_3CCH_3] > \eta^5\text{-}C_5H_5Fe(CO)[P(OC_6H_5)_3] > \eta^5\text{-}C_5H_5Fe(CO)_2$ was established for the reactions of $MCH_2CH{=}CH_2$ with cyano olefins.[6]

In this paper we report the results of a kinetic study of the cycloaddition reaction of various metal-propargyl complexes with $p\text{-}CH_3C_6H_4S(O)_2NCO$ (TSI). The effect on the reactivity of each of the variables, the metal, the ancillary ligands, and the substituent R on the propargyl fragment was measured. The reactivity of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ is compared with that of the corresponding η^1-allyl complexes $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(R){=}C(R')R''$.

Experimental Section

General Procedures. A nitrogen atmosphere was employed routinely in all preparative and kinetic aspects of this work. Ventron neutral alumina, deactivated with 6% (by weight) distilled water, was used in chromatographic separations and purifications. Mass spectra (MS) were recorded by Mr. C. R. Weisenberger on an AEI Model MS-9 spectrometer at 70 eV. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Melting points were taken in evacuated tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on Varian Associates A-60A and EM-360L spectrometers using tetramethylsilane (Me_4Si) as an internal reference. Infrared (IR) measurements were made on Beckman 4250 and IR-9 spectrophotometers using polystyrene film for calibration. The recorded frequencies are accurate to ±2 and ±1 cm^{-1}, respectively. Ultraviolet (UV)-visible spectra were recorded on a Cary 17 spectrophotometer.

Materials. *p*-Toluenesulfonyl isocyanate (TSI), from Aldrich, was distilled at 115 °C (2 torr) before use. 1,1,3-Trichlorotrifluoroacetone, from PCR, Inc., was distilled at 84 °C (760 torr). Other commercially procured reagents were used as received. The propargyl bromides

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and chlorides, $RC\equiv CCH_2X$ (R = CH_3, C_6H_5; X = Br, Cl), were prepared by treatment of the corresponding alcohol, $RC\equiv CCH_2OH$, from Farchan Chemical Co., with PBr_3[13,14] and $SOCl_2$,[15] respectively.

Tetrahydrofuran (THF) and ether were distilled from Na/K alloy at 65 and 34.6 °C, respectively. Toluene (bp 110 °C) was distilled from K_2CO_3, and pentane (bp 36 °C) was distilled from CaH_2. Methylene chloride (bp 40 °C) and chlorobenzene (bp 132 °C) were purified by distillation from P_4O_{10} under nitrogen. Other solvents were of reagent grade or equivalent quality and were used without further purification.

Metal–Propargyl and –η^1-Allyl Complexes. The propargyl complexes η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$ (R = CH_3,[16] C_6H_5[17]), η^5-$C_5H_5Mo(CO)_3CH_2C\equiv CR$ (R = CH_3,[18] C_6H_5[18]), η^5-$C_5H_5Mo(CO)_2(L)CH_2C\equiv CC_6H_5$ (L = $P(C_6H_5)_3$,[19] $P(OC_6H_5)_3$[19]), η^5-$C_5H_5W(CO)_3CH_2C\equiv CC_6H_5$,[20] $Mn(CO)_5CH_2C\equiv CC_6H_5$,[17] and $Mn(CO)_4[P(C_6H_5)_3]CH_2C\equiv CR$ (R = CH_3,[21] C_6H_5[21]) and the η^1-allyl complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R)=C(R')R''$ (R = R′ = R″ = H;[22] R = R′ = H, R″ = CH_3;[22] R = R′ = H, R″ = C_6H_5;[23] R = H, R′ = R″ = CH_3[23]) were prepared by known procedures.

The previously unreported η^5-$C_5H_5Cr(NO)_2CH_2C\equiv CC_6H_5$ was obtained by dropwise addition to η^5-$C_5H_5Cr(NO)_2Cl$ (1.06 g, 5.00 mmol), prepared by the method of King,[24] of $C_6H_5C\equiv CCH_2MgBr$ from Grignard-grade Mg chips (0.344 g, 24.3 mmol) and $C_6H_5C\equiv CCH_2Br$ (2.92 g, 15.0 mmol) in 50 mL of ether. The reaction mixture was stirred at 25 °C for 1.5 h, solvent was evaporated, and the remaining brown tar was extracted first with pentane (5 × 100 mL) and then with 50 mL of 1:5 (v/v) CH_2Cl_2–pentane. The extracts were combined, solvent was evaporated, and the residual brown oil was chromatographed on alumina by eluting with pentane. The yellow band was collected, and the effluent was concentrated to afford gold leaflets of η^5-$C_5H_5Cr(NO)_2CH_2C\equiv CC_6H_5$, which were collected by filtration: mp 76–77 °C; yield 0.38 g (26%); ^{1}H NMR ($CDCl_3$) τ 2.73 (m, C_6H_5), 4.44 (s, C_5H_5), 7.73 (s, CH_2); IR (Nujol) $\nu(C\equiv C)$ 2173 (w), $\nu(N\equiv O)$ 1788 (vs), 1685 (vs) cm^{-1}; MS (60 °C, relative intensities in parentheses) prominent peaks at *m/e* 292 P^+ (47), 262 $(P - NO)^+$ (85), 232 $(P - 2NO)^+$ (224), 177 $(P - C_9H_7)^+$ (18), 167 $(P - 2NO - C_5H_5)^+$ (11), 147 $(P - NO - C_9H_7)^+$ (12), 117 $(P - 2NO - C_9H_7)^+$ (100), 115 $C_9H_7^+$ (91), 52 Cr^+ (100). Anal. Calcd for $C_{14}H_{12}CrN_2O_2$: C, 57.53; H, 4.11. Found: C, 57.81; H, 4.30.

Preparation of $MC=C(C_6H_5)C(CCl_2F)(CClF_2)OCH_2$ (M = η^5-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$, η^5-$C_5H_5Cr(NO)_2$). To a solution of 0.4–0.6 mmol of the metal–propargyl complex in 15–25 mL of CH_2Cl_2 was added excess $Cl_2FCC(O)CClF_2$ (generally 1.0–1.5 g, ca. 5–7 mmol) in ca. 15 mL of CH_2Cl_2. The resulting solution was stirred at 25 °C for 2–3 h, solvent was evaporated, and the residue was dissolved in minimum of 1:1 (v/v) pentane–CH_2Cl_2 and chromatographed on alumina by eluting with the same solvent mixture. The product band was collected, and the effluent was concentrated to induce precipitation of the title complex, which was collected by filtration. Details of the characterization of each product are presented below.

η^5-$C_5H_5Fe(CO)_2C=C(C_6H_5)C(CCl_2F)(CClF_2)OCH_2$: yellow-orange solid; mp 103 °C; 42% yield; ^{1}H NMR ($CDCl_3$) τ 2.67 (m, C_6H_5), 5.13 (s, CH_2), 5.36 (s, C_5H_5); IR (CH_2Cl_2) $\nu(C\equiv O)$ 2025 (vs), 1973 (vs) cm^{-1}; MS (90 °C, relative intensities in parentheses) prominent peaks at *m/e* 506 P^+ (1), 450 $(P - 2CO)^+$ (6), 292 $(P - C_3Cl_3F_3O)^+$ (11), 236 $(P - 2CO - C_3Cl_3F_3O)^+$ (187), 186 $(C_5H_5)_2Fe^+$ (177). Anal. Calcd for $C_{19}H_{12}Cl_3F_3FeO_3$: C, 44.96; H, 2.38; Cl, 20.95. Found: C, 47.73; H, 2.95; Cl, 19.22.

η^5-$C_5H_5Mo(CO)_3C=C(C_6H_5)C(CCl_2F)(CClF_2)OCH_2$: orange solid; mp 183 °C; 58% yield; ^{1}H NMR ($CDCl_3$) τ 2.60 (m, C_6H_5), 4.77 (s, C_5H_5), 5.05 (s, CH_2); IR (CH_2Cl_2) $\nu(C\equiv O)$ 2025 (vs), 1962 (vs), 1939 (vs) cm^{-1}; MS (78 °C, relative intensities in parentheses) prominent peaks at *m/e* 576 P^+ (1), 548 $(P - CO)^+$ (4), 163 $C_5H_5Mo^+$ (2), 115 $C_9H_7^+$ (100). Anal. Calcd for $C_{20}H_{12}Cl_3F_3MoO_4$: C, 41.73; H, 2.10; Cl, 18.47. Found: C, 42.00; H, 2.18; Cl, 18.37.

η^5-$C_5H_5Cr(NO)_2C=C(C_6H_5)C(CCl_2F)(CClF_2)OCH_2$: green solid; mp 145 °C; 64% yield. ^{1}H NMR ($CDCl_3$) τ 2.68 (m, C_6H_5), 4.78 (s, C_5H_5), 4.94 (s, CH_2); IR (CH_2Cl_2) $\nu(N\equiv O)$ 1798 (vs), 1692 (vs) cm^{-1}; MS (80 °C, relative intensities in parentheses) prominent peaks at *m/e* 506 P^+ (35), 490 $(P - O)^+$ (25), 476 $(P - NO)^+$ (76), 375 $(P - NO - CCl_2F)^+$ (33), 259 $(P - C_2ClF_3O - C_9H_7)^+$ (36), 229 $(P - NO - C_2ClF_3O - C_9H_7)^+$ (50), 177 $(P - C_3Cl_3F_3O - C_9H_7)^+$ (60), 115 $C_9H_7^+$ (216), 52 Cr^+ (100). Anal. Calcd for $C_{17}H_{12}Cl_3CrF_3N_2O_3$: C, 40.21; H, 2.36; Cl, 20.96. Found: C, 40.11; H, 2.29; Cl, 20.84.

Preparation of $MC=C(CH_3)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$ (M = η^5-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$, $Mn(CO)_4[P(C_6H_5)_3]$) and $MC=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$ (M = η^5-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$, η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$, η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$, η^5-$C_5H_5W(CO)_3$, $Mn(CO)_5$, $Mn(CO)_4[P(C_6H_5)_3]$, η^5-$C_5H_5Cr(NO)_2$). With the exception of η^5-$C_5H_5Fe(CO)_2C=C(CH_3)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$, which was prepared as described in the literature,[25] all of the title complexes are new. They were synthesized by the following general procedure.

To a solution of 1–4 mmol of the metal–propargyl complex in 5–20 mL of CH_2Cl_2 was syringed a deficiency of TSI (usually ca. 0.5 equiv). The resulting solution was stirred at 25 °C and concentrated. Chromatography on alumina, eluting first with hexane or hexane–CH_2Cl_2 to remove any unreacted propargyl complex and then with CH_2Cl_2, afforded the title complex which precipitated from the effluent on addition of hexane. Alternatively, the reaction solution was filtered, concentrated, and treated with hexane to induce formation of crystalline product. Details of each synthesis, including reaction time (rt), method of purification, percent yield (based on TSI), and elemental analysis, are given below. Spectroscopic data are listed in Table I.

η^5-$C_5H_5Mo(CO)_3C=C(CH_3)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 0.5 h; crystallization; orange solid; mp 167 °C dec; 93% yield. Anal. Calcd for $C_{20}H_{17}MoNO_6S$: C, 48.49; H, 3.46; S, 6.47. Found: C, 48.18; H, 3.45; S, 6.45.

$Mn(CO)_4[P(C_6H_5)_3]C=C(CH_3)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 0.5 h; chromatography; yellow solid; mp 110 °C dec; 37% yield. Anal. Calcd for $C_{34}H_{27}MnNO_7PS$: C, 60.08; H, 4.00. Found: C, 59.89; H, 4.03.

η^5-$C_5H_5Fe(CO)_2C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 4 h; chromatography; yellow-orange solid; mp 212 °C dec; 95% yield. Anal. Calcd for $C_{24}H_{19}FeNO_5S$: C, 58.91; H, 3.91; S, 6.55. Found: C, 59.12; H, 3.73; S, 6.72.

η^5-$C_5H_5Mo(CO)_3C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 8 h; chromatography; orange solid; mp 176 °C dec; 90% yield. Anal. Calcd for $C_{25}H_{19}MoNO_6S$: C, 53.87; H, 3.44; S, 5.74. Found: C, 53.57; H, 3.33; S, 5.38.

η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 0.5 h; chromatography; yellow solid; mp 180 °C dec; 55% yield. Anal. Calcd for $C_{42}H_{34}MoNO_5PS$: C, 63.76; H, 4.36; S, 4.05. Found: C, 63.49; H, 4.37; S, 4.05.

η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 0.75 h; chromatography; yellow foam that could not be crystallized; 37% yield.

η^5-$C_5H_5W(CO)_3C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 5 h; chromatography; yellow-orange solid; mp 195 °C dec; 64% yield. Anal. Calcd for $C_{25}H_{19}NO_6SW$: C, 46.53; H, 2.97. Found: C, 46.33; H, 3.01.

$Mn(CO)_5C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-*p*$]CH_2$: rt 5 h; crystallization; yellow-orange solid; mp 157 °C dec; 52% yield. Anal.

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Table I. Spectroscopic Properties of $MC{=}C(R)C(O)N[S(O)_2C_6H_4CH_3\text{-}p]CH_2$ (II) and $MC(R)C(R')(R'')C(O)N[S(O)_2C_6H_4CH_3\text{-}p]CH_2$ (III)

complex		IR,[a] cm^{-1}			
M	R	$\nu(C{\equiv}O)$ or $\nu(N{\equiv}O)$	$\nu(C{=}O)$	^1H NMR,[b] τ (J, Hz)	UV-visible,[a,c] λ_{max}, nm (ϵ_{max})
η^5-$C_5H_5Mo(CO)_3$ (II)	CH_3	2038 (s), 1960 (vs), 1947 (vs)	1699 (m)	2.06 (d, 14, $^1/_2C_6H_4$), 2.70 (d, 14, $^1/_2C_6H_4$), 4.42 (s, C_5H_5), 5.64 (q, 1.6, CH_2), 7.58 (s, TSI CH_3), 8.26 (t, 1.6, R CH_3)	
$Mn(CO)_4[P(C_6H_5)_3]$[d]	CH_3	2075 (s), 2002 (sh), 1975 (vs), 1967 (s)	1697 (m)	2.19 (d, 15, $^1/_2C_6H_4$), ~2.7 (m, $3C_6H_5$, $^1/_2C_6H_4$), 5.95 (s, CH_2), 7.68 (s, TSI CH_3), 8.14 (s, R CH_3)	
η^5-$C_5H_5Fe(CO)_2$	C_6H_5	2053 (vs), 1985 (vs)	1698 (s)	1.98 (d, 14, $^1/_2C_6H_4$), ~2.7 (m, C_6H_5, $^1/_2C_6H_4$), 5.25 (s, C_5H_5), 5.38 (s, CH_2), 7.57 (s, CH_3)	362 (700), 240 (14 200) [266 (sh), 322 (12 500)]
η^5-$C_5H_5Mo(CO)_3$	C_6H_5	2048 (s), 1970 (vs), 1953 (s)	1708 (s)	1.94 (d, 15, $^1/_2C_6H_4$), ~2.7 (m, C_6H_5, $^1/_2C_6H_4$), 4.58 (s, C_5H_5), 5.41 (s, CH_2), 7.57 (s, CH_3)	275 (sh), 289 (10 800), 322 (sh), 370 (1900) [266 (sh), 315 (3500)]
η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$[e]	C_6H_5	1953 (s), 1868 (vs)	1700 (s)	1.99 (d, 13, $^1/_2C_6H_4$), ~2.7 (m, $4C_6H_5$, $^1/_2C_6H_4$), 5.08 (s, CH_2), 5.42 (d, 1.9, C_5H_5), 7.58 (s, CH_3)	
η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$[f]	C_6H_5	1973 (s), 1894 (vs)	1681 (s)	2.07 (d, 14, $^1/_2C_6H_4$), ~2.7 (m, $4C_6H_5$, $^1/_2C_6H_4$), 5.16 (s, cis C_5H_5), 5.28 (d, 1.6, trans C_5H_5), 5.66 (s, CH_2), 7.59 (s, CH_3)	
η^5-$C_5H_5W(CO)_3$	C_6H_5	2031 (s), 1959 (vs), 1936 (vs)	1700 (s)	2.19 (d, 15, $^1/_2C_6H_4$), ~2.7 (m, C_6H_5, $^1/_2C_6H_4$), 4.68 (s, C_5H_5), 5.41 (s, CH_2), 7.61 (s, CH_3)	285 (9370), 311 (sh), 322 (sh), 362 (1770) [253 (sh), 305 (9210), 383 (836)]
$Mn(CO)_5$	C_6H_5	2149 (s), 2043 (br)	1700 (s)	2.13 (d, 14, $^1/_2C_6H_4$), ~2.7 (m, C_6H_5, $^1/_2C_6H_4$), 5.29 (s, CH_2), 7.57 (s, CH_3)	321 (sh), 391 (320) [254 (sh), 280 (16 600)]
$Mn(CO)_4[P(C_6H_5)_3]$[d]	C_6H_5	2077 (s), 1988 (sh), 1963 (vs)	1702 (m)	~2.7 (m, $4C_6H_5$, C_6H_4), 5.78 (br, CH_2), 7.60 (s, CH_3)	
η^5-$C_5H_5Cr(NO)_2$	C_6H_5	1801 (s), 1698 (vs)	*h*	2.00 (d, 13, $^1/_2C_6H_4$), ~2.7 (m, C_6H_5, $^1/_2C_6H_4$), 4.76 (s, C_5H_5), 5.31 (s, CH_2), 7.59 (s, CH_3)	317 (2470), 462 (1000) [253 (sh), 305 (19 800), 455 (1590)]
η^5-$C_5H_5Fe(CO)_2$ (III)	H $R' = CH_3$[g] $R'' = H$[g]	2008 (vs), 1952 (vs)	1725 (m)	2.06 (d, 9, $^1/_2C_6H_4$), 2.68 (d, 9, $^1/_2C_6H_4$), 5.12 (s, C_5H_5), 5.15 (s, C_5H_5), 5.8–7.1 (m, CH_2, 2CH), 7.58 (s, TSI CH_3), 9.05 (d, 7, R CH_3)[i]	

[a] In CH_2Cl_2 solution. Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder; br, broad. [b] In $CDCl_3$ solution. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [c] Absorptions of the parent $MCH_2C{\equiv}CR$ given in brackets. [d] Cis isomer. [e] Trans isomer. [f] Cis-trans mixture. [g] *E-Z* mixture. [h] Masked by the $\nu_{as}(N{\equiv}O)$ band at 1698 cm^{-1}. [i] Only one R CH_3 signal located possibly owing to the presence of interfering resonances of impurities.

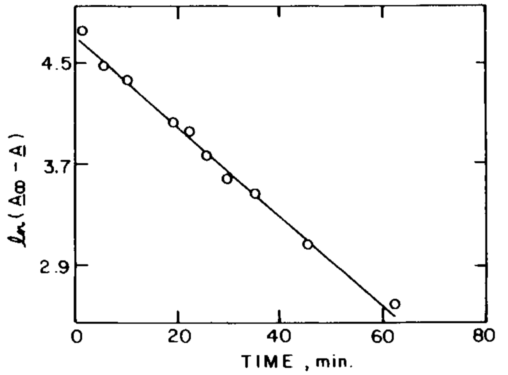


Figure 1. Reaction of η^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$ with a tenfold excess of TSI in CH_2Cl_2 at 25.0 °C.

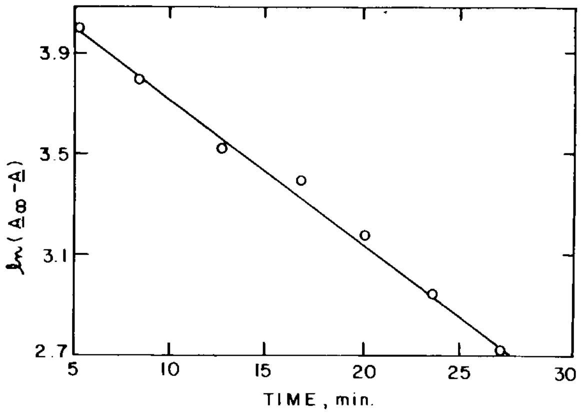


Figure 2. Reaction of η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ in tenfold excess with TSI in CH_2Cl_2 at 25.0 °C.

Calcd for $C_{22}H_{14}MnNO_8S$: C, 52.08; H, 2.78. Found: C, 51.88; H, 2.74.

$Mn(CO)_4[P(C_6H_5)_3]\overline{C{=}C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3\text{-}p]C}H_2$: rt 1 h; crystallization; yellow-orange solid; mp 120 °C dec; 80% yield. Anal. Calcd for $C_{39}H_{29}MnNO_7PS$: C, 63.16; H, 3.94. Found: C, 63.37; H, 4.14.

$\eta^5\text{-}C_5H_5Cr(NO)_2\overline{C{=}C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3\text{-}p]C}H_2$: rt 1 h; crystallization; green solid; mp 256 °C dec; 78% yield. Anal. Calcd for $C_{22}H_{19}CrN_3O_5S$: C, 53.98; H, 3.89; S, 6.34. Found: C, 54.04; H, 4.07; S, 6.42.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C(R)C(R')(R'')C(O)N[S(O)_2C_6H_4CH_3\text{-}p]C}H_2$ ($R = R' = R'' = H$; $R = R' = H$, $R'' = CH_3$; $R = R' = H$, $R'' = C_6H_5$; $R = H$, $R' = R'' = CH_3$). With the exception noted below, these complexes were first prepared by Rosenblum et al.,[5] whose procedure was employed in this work.

$\eta^5\text{-}C_5H_5Fe(CO)_2\overline{CHCH(CH_3)C(O)N[S(O)_2C_6H_4CH_3\text{-}p]C}H_2$ was obtained by the addition of a deficiency of TSI (0.56 mL, 3.68 mmol) to $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (0.991 g, 4.27 mmol) in 15 mL of CH_2Cl_2. The resulting solution was stirred at 25 °C for 2 h and then treated with pentane (200 mL) to precipitate yellow crystals, which were collected by filtration; mp 138 °C dec. Additional product was obtained on concentration of the filtrate; total yield 1.493 g (94%). Anal. Calcd for $C_{19}H_{19}FeNO_5S$: C, 53.15; H, 4.47. Found: C, 52.92; H, 4.64. Spectroscopic data are given in Table I.

General Kinetic Procedures. The kinetic studies of the reactions of metal–propargyl and $-\eta^1$-allyl complexes with TSI were carried out with use of round-bottom flasks containing a magnetic stirring bar. The neck of the flask was fitted with a serum cap, and the flask was wrapped in aluminum foil for protection from light. A freshly chromatographed propargyl or η^1-allyl complex was weighed in the flask under nitrogen, and to it was syringed distilled CH_2Cl_2 (or, in some experiments, toluene, chlorobenzene, or CH_3CN). The flask was reweighed to determine accurately the volume of added CH_2Cl_2 (density = 1.327 g/mL[26]) and then placed in a constant-temperature bath. After thermal equilibrium had been reached, freshly distilled TSI at the same temperature was injected into the flask with a syringe. Following this addition, the reaction solution was kept in the thermostated bath (±0.1 °C), generally at 25.0 °C, with magnetic stirring.

Rates of the reactions were for the most part determined by monitoring the appearance of the lactam $\nu(C{=}O)$ band at ca. 1700 cm^{-1} on a Beckman 4250 infrared spectrophotometer. However, the reaction between $\eta^5\text{-}C_5H_5Cr(NO)_2CH_2C{\equiv}CC_6H_5$ and TSI was followed by measuring the growth of the higher frequency $N{\equiv}O$ stretching absorption, $\nu_s(N{\equiv}O)$, of the organochromium product at 1801 cm^{-1}, since the $\nu(C{=}O)$ band appears to be hidden under the $\nu_{as}(N{\equiv}O)$ absorption at 1698 cm^{-1} (in CH_2Cl_2 solution). Absorbance readings of the appropriate infrared band were made on the reaction solution by withdrawing samples with a syringe at regular time intervals, generally every 3–5 min. Matched infrared cells of various thickness (0.6–2.0 mm) were employed.

All reactions were run under pseudo-first-order conditions, generally with the concentration of TSI in at least a tenfold excess over that of the metal complex. They were usually followed for 10 half-lives.

Treatment of Data. From the infrared spectroscopic data pseudo-first-order rate constants, k_{obsd}, were obtained by graphing ln $(A_\infty - A)$ vs. time, where A_∞ is the absorbance of the organometallic product at infinite time (experimentally, after 10 half-lives) and A is the absorbance of the product at any time of the reaction. For these plots, the values of A and A_∞ were taken to be proportional to the measured peak heights. Very good linear plots ($R^2 > 0.99$) were obtained on this basis. Beer's law, shown previously to hold for the $\nu_{as}(C{\equiv}O)$ absorption of several $\eta^5\text{-}C_5H_5Fe(CO)_2R$ complexes,[27] was assumed to be valid for all of the organometallic products in this study.

Results

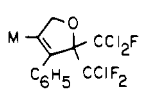
Screening of Electrophilic Reagents. As indicated in the Introduction, a number of electrophilic molecules have been shown to undergo cycloaddition reactions with transition metal–propargyl complexes prior to this study. However, these reactions were conducted under synthetic conditions and provided little basis for comparison of the relative reactivities of different electrophiles.

It was therefore essential to test the behavior of representative electrophilic reagents toward the propargyl complexes before a kinetic study could be commenced. Such a screening was conducted with a view to finding an electrophile that would react cleanly, at a rate measurable by infrared, ultraviolet–visible, or ^1H NMR spectroscopy at ambient temperatures. Generally, a tenfold excess of the electrophilic reagent over the metal complex in CH_2Cl_2 solution was employed. Characterization of the products was usually not attempted if the reaction proved unsuitable for a kinetic study.

Of the tested olefins, TCNE[5,7] reacts rapidly with $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ even at ca. −78 °C. Additionally, the cycloaddition reaction is complicated by the formation of $TCNE^{-\cdot}$, possibly through oxidation of the adduct $\eta^5\text{-}C_5H_5Fe(CO)_2\overline{C{=}C(C_6H_5)C(CN)_2C(CN)_2C}H_2$ by excess TCNE. The olefins $Cl_2C{=}CCl_2$, $(C_6H_5)_2C{=}C(CN)_2$, and $o\text{-}ClC_6H_4CH{=}C(CN)_2$ show no apparent reaction with $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ at 25 °C. It is noteworthy that, in contrast, $o\text{-}ClC_6H_4CH{=}C(CN)_2$ undergoes cycloaddition reaction with iron–η^1-allyl complexes under similar conditions.[5]

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone reacts rapidly with $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ in $CHCl_3$ at room temperature, and with the former complex even at ca. −78 °C. The less electrophilic tetrachloro-1,4-benzoquinone undergoes very slow reaction with $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ at 25 °C; however, this reaction is complicated by low solubility of the quinone in partially chlorinated hydrocarbon solvents and by the instability of the cycloadduct. 1,4-Benzoquinone does not react under these conditions.

Hexafluoroacetone readily affords cycloaddition products on treatment with metal–propargyl complexes either in neat form or in solution.[8] However, the gaseous nature of $(CF_3)_2CO$ (bp −27 °C) suggested that the closely related, but liquid (bp 84 °C), $Cl_2FCC(O)CClF_2$ might be easier to manipulate in kinetic studies. Synthetic-scale reactions between $Cl_2FCC(O)CClF_2$ and each of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, and $\eta^5\text{-}C_5H_5Cr(NO)_2CH_2C{\equiv}CC_6H_5$ ($MCH_2C{\equiv}CC_6H_5$) resulted in the preparation of the expected cycloadducts $M\overline{C{=}C(C_6H_5)C(CCl_2F)(CClF_2)OC}H_2$ (I). The synthesis and characterization of these products, which bear strong similarities to the previously reported[8] complexes $M\overline{C{=}C(C_6H_5)C(CF_3)_2OC}H_2$, are detailed in the Experimental Section. However, when reaction of $Cl_2FCC(O)CClF_2$ with $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ was followed by ^1H NMR spectroscopy, a resonance was noted at τ 6.04 which is due to $Cl_2FCC(OH)_2CClF_2$. All attempts at removal of this diol from the acetone proved unsuccessful, thus precluding the use of $Cl_2FCC(O)CClF_2$ for kinetic studies.



I

Isocyanates comprised a final class of electrophiles that were subjected to the screening. The previously investigated $ClS(O)_2NCO$[5,9] cycloadds rapidly, with accompanying side reactions, to the propargyl fragment of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$ at room temperature. The corresponding reactions of $Cl_3CC(O)NCO$ occur at conveniently measurable rates, but the

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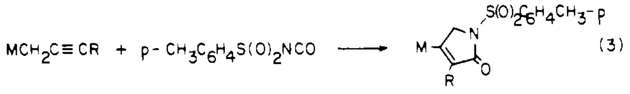
[26] "Handbook of Chemistry and Physics", 52nd ed.; Chemical Rubber Co.: Cleveland, Ohio, 1971–1972; p C-367.

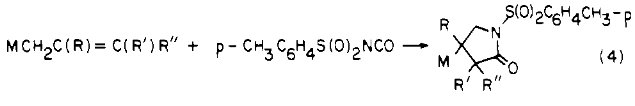
[27] Dizikes, L. J.; Wojcicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 5295.

products decompose gradually in solution. In contrast to the foregoing, TSI reacts with the propargyl complexes to give the cycloadducts cleanly, at a measurable rate by infrared spectroscopy at ambient temperatures. It was accordingly selected for a kinetic study.

Preparation and Characterization of Lactam Cycloaddition Products. Reactions of TSI with transition metal–propargyl and –η^1-allyl complexes proceed according to eq 3 and 4 to



II



III

afford the lactam cycloaddition products, II and III, respectively. These products are most conveniently isolated pure when a deficiency of TSI is employed in the reaction. Under such conditions, more polar II and III can be readily separated from the corresponding unreacted metal–propargyl or –η^1-allyl complex by crystallization or chromatography on alumina. Generally, crystallization leads to a higher yield of the adduct, as chromatography causes decomposition in some cases. Pertinent details are provided in the Experimental Section.

Complexes II were isolated as air-stable solids which analyze satisfactorily for 1:1 adducts of the two reactants. The mass spectrum of η^5-$C_5H_5Fe(CO)_2C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-$p]CH_2$ displays peaks due to $(P - CO)^+$ and $(P - 2CO)^+$, as well as a peak of a substituted ferrocenium ion, η^5-$C_5H_5Fe\{\eta^5$-$C_5H_4C=C(C_6H_5)C(O)N[S(O)_2C_6H_4$-$CH_3$-$p]CH_2\}^+$, but not of the parent ion, P^+. The mass spectrum of η^5-$C_5H_5Cr(NO)_2C=C(C_6H_5)C(O)N[S(O)_2$-$C_6H_4CH_3$-$p]CH_2$ shows the presence of P^+, $(P - NO)^+$, and $(P - 2NO)^+$.

Other spectroscopic properties of II are furnished in Table I. The infrared $\nu(C{\equiv}O)$ and $\nu(N{\equiv}O)$ absorptions are in the range previously reported for cycloadducts derived from transition metal–propargyl complexes and various unsaturated electrophilic molecules.[2,5,7-10] With the exception of η^5-$C_5H_5Cr(NO)_2C=C(C_6H_5)C(O)N[S(O)_2C_6H_4CH_3$-$p]CH_2$, all complexes exhibit a medium-to-strong-intensity lactam $\nu(C{=}O)$ band at 1708–1681 cm^{-1}. For the chromium complex, this absorption appears to be hidden under the $\nu_{as}(N{\equiv}O)$ band at 1698 cm^{-1}, which is substantially stronger than the $\nu_s(N{\equiv}O)$ band at 1801 cm^{-1}. The ^1H NMR spectra in Table I display no unusual features, being entirely consistent with the assigned structures II. This structural assignment is strictly analogous to that made earlier for the products of reaction of metal–propargyl complexes with $ClS(O)_2NCO$.[9] The previously reported[25] adduct of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ and TSI was also accorded structure II.

The only new cycloadduct of type III resulted from reaction of TSI with η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$. It was characterized by elemental analysis and infrared and ^1H NMR spectroscopy (Table I). These data are in full accord with structure III, which was earlier assigned to the products of reaction of TSI with several strictly analogous iron–η^1-allyl complexes.[5,25] Other electrophilic isocyanates, including $ClS(O)_2NCO$, $Cl_3CC(O)NCO$, and $(2,5$-$C_6H_3Cl_2)NCO$, afford similar lactam adducts.[5,9,25]

Kinetic Determinations. Kinetic data were obtained by infrared spectroscopy for the reactions in eq 3 and 4 under pseudo-first-order conditions, with TSI or, in some cases, the organometallic complex in a tenfold excess over the other reactant in CH_2Cl_2 at 25.0 °C. ^1H NMR spectroscopy was employed to determine relative rate constants in special cases which will be considered later. However, no absolute rate data were obtained by this method, since most reactions proceed very rapidly at ambient temperatures and the generally required higher concentrations of the reactants. Ultraviolet–visible spectroscopy was considered but not adopted, as the spectra of $MC=C(R)C(O)N[S(O)_2C_6H_4CH_3$-$p]CH_2$ and the precursors $MCH_2C{\equiv}CR$, included in Table I, generally show relatively small differences. This method appeared feasible only for the reactions of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ and η^5-$C_5H_5Cr(NO)_2CH_2C{\equiv}CC_6H_5$.

Except as noted later, all reactions appear to proceed cleanly and directly to the cycloadducts. No side products were observed and, even at −78 °C, no intermediates were detected by ^1H NMR spectroscopy.

For the runs with TSI at 2×10^{-2} to 2.0 M in a tenfold excess over the organometallic reactant (MR), plots of ln $(A_\infty - A)$ vs. time are linear and thus consistent with the rate law

$$d[\text{cycloadduct}]/dt = k_{obsd}[\text{MR}] \qquad (5)$$

where

$$k_{obsd} = k[\text{TSI}]^n \qquad (6)$$

A typical plot is shown in Figure 1 for η^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$.

When reactions were run with the metal complex in tenfold excess at 0.2–1.0 M, plots of ln $(A_\infty - A)$ vs. time also showed linearity, being in accord with the rate law

$$d[\text{cycloadduct}]/dt = k'_{obsd}[\text{TSI}] \qquad (7)$$

where

$$k'_{obsd} = k[\text{MR}]^n \qquad (8)$$

A representative graph is given in Figure 2 for η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$.

The foregoing results indicate that the cycloaddition is first order in each reactant and second order overall; i.e., the value of n in eq 6 and 8 equals 1:

$$d[\text{cycloadduct}]/dt = k[\text{MR}][\text{TSI}] \qquad (9)$$

This rate law is further supported by a close similarity (within 10%) of k_{obsd} and k'_{obsd} for runs employing excess TSI and excess metal complex, respectively, in same concentrations.

The second-order rate coonstants, k, for the cycloaddition reactions of metal–propargyl and –η^1-allyl complexes with TSI in CH_2Cl_2 at 25.0 °C are compiled in Table II. Each of these values represents the average of ca. four determinations, the agreement among which is indicated in the table.

A few of the reactions studied require special comments. The complex η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$,[19] present as the trans isomer, affords the trans cycloadduct exclusively, as inferred by examination of the ^1H NMR spectrum of the product. The related η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CC_6H_5$,[19] an approximately 1.7:1.0 trans–cis mixture which does not appear to change on the time scale of the experiment, reacts with TSI to yield an adduct of ca. 7:1 trans–cis isomeric composition. Good linear plots of ln $(A_\infty - A)$ vs. time were obtained by infrared spectroscopy for the latter reaction.

Cycloaddition between η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ and TSI was examined to elucidate the relative reactivities of the E and Z isomers of the η^1-allyl complex. A 1.8:1.0 E–Z mixture of the organoiron complex (1.3 M) was allowed to react with a deficiency (0.54 equiv) of TSI in CH_2Cl_2, and unreacted η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ was then separated from the cycloadduct by chromatography on alumina.

Table II. Second-Order Rate Constants for the Cycloaddition Reactions of $MCH_2C\equiv CR$ and $MCH_2C(R)=C(R')R''$ with TSI in CH_2Cl_2 at 25.0 °C

complex				10^2k,[a]	
M	R	R'	R''	$M^{-1}\ s^{-1}$	rel *k*
$Mn(CO)_4[P(C_6H_5)_3]$	CH_3			$\gtrsim 20$[b]	$\gtrsim 3000$
$\eta^5\text{-}C_5H_5Fe(CO)_2$	CH_3			6.3	1000
$\eta^5\text{-}C_5H_5Mo(CO)_2\text{-}[P(C_6H_5)_3]$	C_6H_5			3.3	540
$\eta^5\text{-}C_5H_5Mo(CO)_3$	CH_3			2.1	340
$Mn(CO)_4[P(C_6H_5)_3]$	C_6H_5			0.77	130
$\eta^5\text{-}C_5H_5Mo(CO)_2\text{-}[P(OC_6H_5)_3]$	C_6H_5			0.66	110
$\eta^5\text{-}C_5H_5Cr(NO)_2$	C_6H_5			0.63[c]	100
$\eta^5\text{-}C_5H_5Fe(CO)_2$	C_6H_5			0.21	34
$\eta^5\text{-}C_5H_5Mo(CO)_3$	C_6H_5			0.070	11
$\eta^5\text{-}C_5H_5W(CO)_3$	C_6H_5			0.027	4.4
$Mn(CO)_5$	C_6H_5			0.0061	1.0
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	CH_3	11[d]	1800
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	CH_3	CH_3	7.2	1200
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	H	0.26	43
$\eta^5\text{-}C_5H_5Fe(CO)_2$	H	H	C_6H_5	0.25	41

[a] ±10% or better for $MCH_2C\equiv CR$ and ±6% for $MCH_2C(R)=C(R')R''$ unless noted otherwise. [b] Estimated value; see the text. [c] ±13%. [d] For an *E-Z* mixture; see the text.

Table III. Second-Order Rate Constants for the Cycloaddition Reaction of $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_3$ with TSI in Toluene

temp, °C	10^2k,[a] $M^{-1}\ s^{-1}$	temp, °C	10^2k,[a] $M^{-1}\ s^{-1}$
25.0	1.1[b]	39.8	2.6
30.0	1.4	46.6	3.9

[a] ±6% unless noted otherwise. [b] ±8%.

The ^1H NMR spectrum showed the unreacted complex to be 2.9:1.0 *E-Z*. Thus, the ratio of the rate constants, k_Z/k_E, is 2.0.[28] Since the starting isomeric mixture of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH=CHCH_3$ reacts rather rapidly ($t_{1/2} \approx 2$ min) with TSI, only a small number of readings could be taken by infrared spectroscopy. As a result, even though the two isomers differ in reactivity, the expected nonlinearity of the graph of ln $(A_\infty - A)$ vs. time was not observed.

The manganese complex $Mn(CO)_5CH_2C\equiv CC_6H_5$ undergoes cycloaddition slowly, and after ca. 8 h (<5 half-lives) decomposition of the product becomes noticeable. The final readings (A_∞) were obtained on freshly prepared solutions of the adduct of the appropriate concentrations. By contrast, the reaction of the phosphine-substituted $Mn(CO)_4[P(C_6H_5)_3]CH_2C\equiv CCH_3$ with excess TSI is essentially complete in 3 min. Hence the rate constant in Table II is only a rough estimate.

The relative rate constants for the cycloaddition of TSI to $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ and $\eta^5\text{-}C_5H_5Cr(NO)_2CH_2C\equiv CC_6H_5$ were compared by ^1H NMR spectroscopy. A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ (0.41 M), $\eta^5\text{-}C_5H_5Cr(NO)_2CH_2C\equiv CC_6H_5$ (0.15 M), and TSI (0.10 M) in $CDCl_3$ was stored for 0.5 h at 25 °C, after which time the concentrations of the four organometallic species were determined by integration of the C_5H_5 resonances. A ratio, $k_{Cr}/k_{Fe} = 2.5$, was obtained on this basis.[28] This value may be compared with $k_{Cr}/k_{Fe} = 3.0$ obtained by infrared spectroscopy in CH_2Cl_2 at 25.0 °C.

The dependence of the rate constant on temperature was determined for the reaction of $\eta^5\text{-}C_5H_5Mo(CO)_2CH_2C\equiv CCH_3$ with TSI in toluene at 25.0–46.6 °C. From the data contained in Table III the activation parameters $E_a = 11.5$ kcal/mol, $\Delta H^\ddagger = 10.9$ kcal/mol, and $\Delta S^\ddagger = -31$ eu were calculated.

Table IV. Second-Order Rate Constants for the Cycloaddition Reactions of $MCH_2C\equiv CR$ with TSI at 25.0 °C

complex			10^2k,[a]	ϵ (temp,
M	R	solvent	$M^{-1}\ s^{-1}$	°C)[b]
$\eta^5\text{-}C_5H_5Mo(CO)_3$	CH_3	toluene	1.1	2.38 (25)
$\eta^5\text{-}C_5H_5Mo(CO)_3$	CH_3	chlorobenzene	1.7	5.62 (25)
$\eta^5\text{-}C_5H_5Mo(CO)_3$	CH_3	CH_2Cl_2	2.1	8.93 (25)
$\eta^5\text{-}C_5H_5Fe(CO)_2$	C_6H_5	CH_2Cl_2	0.63	8.93 (25)
$\eta^5\text{-}C_5H_5Fe(CO)_2$	C_6H_5	CH_3CN	1.2	37.5 (20)

[a] ±10% or better. [b] From: Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Weissberger, A., Ed; Wiley-Interscience: New York, 1970.

The influence of solvent on the rate of cycloaddition was examined for $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_3$ in toluene and chlorobenzene in addition to CH_2Cl_2. Because this reaction is already quite rapid in CH_2Cl_2, the effect of a more polar solvent, CH_3CN, was tested instead on the less reactive $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$. The appropriate rate constants are given in Table IV.

Discussion

Since no intermediates could be detected, the reactions in eq 3 and 4 appear to proceed by one of two general mechanisms. They may follow a two-step pathway shown in eq 1 and 2, with the second step being much faster than the first. Alternatively, they take place in a concerted fashion.

The small $\Delta H^\ddagger$ (10.9 kcal/mol) and the large negative $\Delta S^\ddagger$ (−31 eu) for the reaction of $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_3$ with TSI do not distinguish between the foregoing mechanisms for the propargyl complexes. However, a differentiation between dipolar (or ionic) and nonpolar reaction pathways can often be made by examining the dependence of the rate constant on the nature of the solvent.[29] In the present study, only a twofold increase in *k* obtains for the reaction of $\eta^5\text{-}C_5H_5Mo(CO)_3CH_2C\equiv CCH_3$ with TSI as the solvent changes from toluene ($\epsilon = 2.38$) to CH_2Cl_2 ($\epsilon = 8.93$). A comparable increase in *k* is observed for the cycloaddition between $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ and TSI on going from CH_2Cl_2 to CH_3CN ($\epsilon = 37.5$). Such small changes indicate a relatively nonpolar transition state which would be consistent with a concerted process for the cycloaddition reaction in eq 3. However, these rate data are not incompatible with the alternative, two-step pathway. Reactions between two uncharged species to give ionic products may exhibit a small solvent effect on rate if the transition state is developed early along the reaction coordinate.[30] Such a situation apparently exists for the reaction of $(C_2H_5)_3N$ with C_2H_5I to give $(C_2H_5)_4N^+I^-$ (Menshutkin reaction). There the relative rate constants (at 30 °C) in the solvents chlorobenzene, CH_2Cl_2, and C_2H_5CN are 1.0, 4.3, and 6.1, respectively.[31] Similarly, the reaction between $Ir(CO)[P(C_6H_5)_3]_2Cl$ and CH_3I, which initially affords $Ir(CO)[P(C_6H_5)_3]_2(CH_3)Cl^+I^-$, experiences only ca. tenfold rate acceleration on changing the solvent from benzene to dimethylformamide.[32]

Because of the foregoing considerations we cannot determine unambiguously whether the reaction in eq 3 proceeds via a dipolar intermediate or in a concerted fashion. However, previous stereochemical work on the cycloaddition between transition metal–propargyl complexes and $CF_3(CN)C=C(CN)CF_3$ ruled out a concerted mechanism for that reaction.[3] We therefore assume that the reaction in point entails a two-step process depicted in eq 1. The corresponding cyclo-

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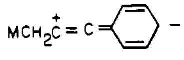
addition of the η^1-allyl complexes and TSI (eq 4) is thought to involve a parallel mechanism (eq 2). Zwitterionic intermediates were detected and intercepted in the reaction of η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}C(R')R''$ with SO_2.[11,12]

Before discussing the rate data compiled in Table II, we wish to address the question of reversibility of the two steps comprising the reactions in eq 1 and 2. With the exception of the adducts derived from the propargyl complexes and SO_2 which revert to the reactants under certain conditions,[16] these cycloaddition products display no apparent tendency to dissociate into their components at ambient temperatures.[7-10,12] Thus, the two steps of eq 1 and 2 are not *both* readily reversible. However, it cannot be determined whether the first or second step *alone* is reversible for the reactions examined in this study. Since carbon–carbon bonds are generally kinetically stable, we assume that each of the two steps shows little, if any, propensity for back-reaction. This would mean that the rate constants in Table II refer to the formation of the zwitterion (the first step) and are free of equilibrium complications.

The aforementioned rate constants span a range of ca. 3000 for the different propargyl complexes ($MCH_2C{\equiv}CR$) examined. For the unsubstituted metal carbonyl and cyclopentadienylmetal carbonyl and nitrosyl complexes, the value of k decreases in the order M = η^5-$C_5H_5Cr(NO)_2$ > η^5-$C_5H_5Fe(CO)_2$ > η^5-$C_5H_5Mo(CO)_3$ > η^5-$C_5H_5W(CO)_3$ > $Mn(CO)_5$ when R = C_6H_5 and in the order M = η^5-$C_5H_5Fe(CO)_2$ > η^5-$C_5H_5Mo(CO)_3$ when R = CH_3. Interestingly, the relationship M = η^5-$C_5H_5Cr(NO)_2$ > η^5-$C_5H_5Fe(CO)_2$ is the opposite of that found for the reaction of the corresponding η^1-allyl complexes, $MCH_2CH{=}CH_2$, with *o*-$ClC_6H_4CH{=}C(CN)_2$.[5] However, exactly the same order was observed for sulfur dioxide insertion, M = η^5-$C_5H_5Cr(NO)_2R$ > η^5-$C_5H_5Fe(CO)_2R$ when R = $CH_2C_6H_5$ and C_6H_5.[33] This order may result from a lower formal oxidation state of chromium(0) than of iron(II). In the case under investigation, a more negative chromium(0) can accelerate the reaction by (1) increasing electron density at the propargyl $C{\equiv}C$ and thus making it more susceptible to attack by the electrophilic TSI, (2) weakening the M—C σ bond and promoting a σ-to-π rearrangement, and (3) stabilizing the incipient metal–η^2-allene bond through greater π back-donation. Of course, some of these effects are not readily separable, and their relative contributions cannot be evaluated. It is also to be noted that the order M = η^5-$C_5H_5Mo(CO)_3$ > η^5-$C_5H_5W(CO)_3$ holds for the reactions of the corresponding η^1-allyl[23] and alkyl[33] complexes with other electrophiles such as SO_2.

Replacement of a carbonyl ligand in $MCH_2C{\equiv}CC_6H_5$ (M = $Mn(CO)_5$ or η^5-$C_5H_5Mo(CO)_3$) with $P(C_6H_5)_3$ or $P(OC_6H_5)_3$ leads to a substantial increase in the rate of the cycloaddition reaction. Thus, M = $Mn(CO)_4[P(C_6H_5)_3]$ > $Mn(CO)_5$ and M = η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$ > η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$ > η^5-$C_5H_5Mo(CO)_3$. Since σ-donor strength of the relevant ligands follows the order $P(C_6H_5)_3$ > $P(OC_6H_5)_3$ > CO,[34] the increase in k parallels an increase in electron density at the metal. Thus, the observed rate acceleration can be rationalized in the same manner as for η^5-$C_5H_5Cr(NO)_2$ vis-à-vis η^5-$C_5H_5Fe(CO)_2$. A similar trend was noted for the rate of the cycloaddition between η^5-$C_5H_5Fe(CO)(L)CH_2CH{=}CH_2$ and cyano olefins, viz., L = $P(OCH_2)_3CCH_3$ > $P(OC_6H_5)_3$ > CO.[6] Furthermore, electrophilic attack of SO_2 at η^5-$C_5H_5Fe(CO)(L)CH_3$ follows the order L = $P(n\text{-}C_4H_9)_3$ > $P(C_6H_5)_3$ > CO.[35]

For a given metal and ancillary ligands, the rate constant depends on the propargyl substituent, R, and decreases from R = CH_3 to R = C_6H_5. Thus, for $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CR$, $k_{CH_3}/k_{C_6H_5}$ = 16, and for each of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ and η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CR$, $k_{CH_3}/k_{C_6H_5}$ = 30. The faster reaction of the methylpropargyl complexes than of the corresponding phenylpropargyl complexes accords with both steric and electronic properties of the two substituents. A contributing resonance structure, IV, would deactivate the $C{\equiv}C$ bond of the phenylpropargyl complex relative to that of the methylpropargyl complex to attack by TSI.



IV

A similar comparison of the η^1-allyl complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}C(R')R''$ affords the following order of reactivity as a function of the substrate ligand: $CH_2CH{=}CHCH_3$ (relative k = 1800) > $CH_2CH{=}C(CH_3)_2$ (relative k = 1200) > $CH_2CH{=}CH_2$ (relative k = 43) $\gtrsim$ $CH_2CH{=}CHC_6H_5$ (relative k = 41). With the exception of the cinnamyl complex, which shows an unexpectedly fast reaction when compared with the allyl complex, the foregoing order is readily explicable by a combination of electronic and steric effects. The presence of the electron-releasing CH_3 group(s) apparently activates the η^1-allyl C=C bond to attack by the electrophilic TSI, since both the crotyl and the 3-methyl-2-butenyl complexes react substantially faster than the allyl complex. The importance of steric effects is demonstrated by the somewhat greater reactivity of the crotyl complex than of the 3-methyl-2-butenyl complex. Additionally, the less hindered *Z* isomer of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ undergoes cycloaddition twice as rapidly as the more encumbered *E* isomer.

It is of some interest to compare the reactivities of the analogous, structurally related propargyl and η^1-allyl complexes. Surprisingly, these reactivities are very similar. Accordingly, η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (relative k = 34) cycloadds TSI at about the same rate as does η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$ (relative k = 41), and the reactivity of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ (relative k = 1,000) is close to that of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (relative k = 1800).

The foregoing behavior contrasts with that of organic olefins and acetylenes toward electrophiles. The olefins display greater reactivity than the structurally related acetylenes;[36] e.g., reaction with bromine of $C_6H_5CH{=}CHC_6H_5$ proceeds 250 times as rapidly as that of $C_6H_5C{\equiv}CC_6H_5$.[37] The difference may be ascribed to higher ionization energies of the π electrons of the acetylenes compared to those of the olefins.[38]

The observed similarity in reactivity of the structurally related propargyl and η^1-allyl complexes toward TSI is not general among electrophiles undergoing cycloaddition according to eq 1 and 2. In fact, *o*-$ClC_6H_4CH{=}C(CN)_2$ and $NCC{\equiv}CCN$ react readily with the η^1-allyl complexes[5,21] but not with the propargyl complexes.[21] At the other extreme of the relative reactivity scale are SO_2, which reacts rapidly with η^5-$C_5H_5W(CO)_3CH_2C{\equiv}CR$[20] but very slowly (and with insertion) with η^5-$C_5H_5W(CO)_3CH_2C(R){=}C(R')R''$,[23] and neat $(CF_3)_2CO$, which cycloadds to η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ but not to η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}C(R')R''$.[18] Clearly, selectivity of electrophiles to attack at the propargyl or the η^1-allyl fragment is an important but as yet poorly understood feature of the cycloaddition reaction.

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Conclusion

The present study has elucidated several structure–reactivity relationships in the [3+2] cycloaddition reaction between transition metal–propargyl complexes and TSI. Accordingly, the bimolecular rate constant is sensitive to the nature of the metal together with its ancillary ligands (η^5-$C_5H_5Cr(NO)_2$ > η^5-$C_5H_5Fe(CO)_2$ > η^5-$C_5H_5Mo(CO)_3$ > η^5-$C_5H_5W(CO)_3$ > $Mn(CO)_5$) and particularly sensitive to replacement of CO with stronger bases (i.e., L = $P(C_6H_5)_3$ > $P(OC_6H_5)_3$ > CO). Methylpropargyl complexes react considerably faster than the corresponding phenylpropargyl complexes. Interestingly and perhaps fortuitously, analogous, structurally related iron–propargyl and –η^1-allyl complexes cycloadd at comparable rates. The cycloaddition reaction shows a small solvent effect and exhibits a large negative ΔS^*. It was not possible unequivocally to distinguish between a two-step dipolar mechanism and a concerted one from these data alone.

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Registry No. I (M = η^5-$C_5H_5Fe(CO)_2$), 76514-46-0; I (M = η^5-$C_5H_5Mo(CO)_3$), 76498-72-1; I (M = η^5-$C_5H_5Cr(NO)_2$), 76498-73-2; II (M = η^5-$C_5H_5Fe(CO)_2$, R = CH_3), 40695-14-5; II (M = η^5-$C_5H_5Mo(CO)_3$, R = CH_8), 76498-74-3; II (M = $Mn(CO)_4[P(C_6H_5)_3]$, R = CH_3), 76498-75-4; II (M = η^5-$C_5H_5Fe(CO)_2$, R = C_6H_5), 76498-76-5; II (M = η^5-$C_5H_5Mo(CO)_3$, R = C_6H_5), 76498-77-6; II (M = η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]$, R = C_6H_5), 76498-78-7; II (M = η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$, R = C_6H_5) (cis isomer), 76498-79-8; II (M = η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$, R = C_6H_5) (trans isomer), 76549-10-5; II (M = η^5-$C_5H_5W(CO)_3$, R = C_6H_5), 76498-80-1; II (M = $Mn(CO)_5$, R = C_6H_5), 76498-81-2; II (M = $Mn(CO)_4[P(C_6H_5)_3]$, R = C_6H_5), 76498-82-3; II (M = η^5-$C_5H_5Cr(NO)_2$, R = C_6H_5), 76498-83-4; III (M = η^5-$C_5H_5Fe(CO)_2$, R = R′ = H, R″ = CH_3) (trans isomer), 76514-47-1; III (M = η^5-$C_5H_5Fe(CO)_2$, R = R′ = H, R″ = CH_3) (cis isomer), 76581-97-0; η^5-$C_5H_5Cr(NO)_2CH_2C{\equiv}CC_6H_5$, 76498-84-5; $Cl_2FCC(O)CClF_2$, 79-52-7; TSI, 4083-64-1; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, 34822-36-1; η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CCH_3$, 32877-61-5; η^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, 32877-62-6; η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 54775-72-3; η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 69372-50-5; η^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$, 32993-03-6; $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, 23626-46-2; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CCH_3$, 64070-51-5; $Mn(CO)_4[P(C_6H_5)_3]CH_2C{\equiv}CC_6H_5$, 64070-52-6; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$, 38960-10-0; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (*E* isomer), 56389-74-3; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, 31798-46-6; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, 38905-70-3; η^5-$C_5H_5Cr(NO)_2Cl$, 12071-51-1; η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (*Z* isomer), 56389-75-4.

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Reactions of Protic Acids with a Hydridoorganometal Cluster: $HRu_3(CO)_9(C_2C(CH_3)_3)$

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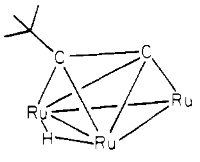
The titrations of $HRu_3(CO)_9C_6H_9$ (I), $HRu_3(CO)_8(C_6H_9)PR_3$ (R = C_6H_5, OCH_3) (II), and $HRu_3(CO)_7(C_6H_9)(PR_3)_2$ (R = C_6H_5, OCH_3) (III) with CF_3SO_3H in CD_2Cl_2 have been followed by variable-temperature ^1H NMR. Initial protonation takes place at the metal core, but significant differences in the relative basicities and the rates of *inter*- and *intra*molecular hydride exchange are observed. In neat sulfuric acid a second protonation of I takes place at the organic ligand to yield a dicationic dihydrido complex $H_2Ru_3(CO)_9(HC{=}CC(CH_3)_3)^{2+}$. In the case of II two isomeric dications are obtained as kinetic products with subsequent rearrangement to the more thermodynamically stable isomer. In D_2SO_4 II gives only the more thermodynamically stable product while deuterated II in H_2SO_4 gives a different isomer ratio than II in H_2SO_4. A mechanism explaining this unusual deuterium isotope effect is presented and discussed.

Introduction

Dynamic NMR studies of the reactions of protic acids with low oxidation state mononuclear organometallic complexes have yielded much useful information about the basicity of different types of organo transition metal compounds.[1] Direct protonation of the metal atom has been demonstrated for many complexes by using NMR techniques. The transition metal "hydride" bond may be long-lived as in the case for π-arene complexes[2] or may be a short-lived intermediate as has been invoked in acid cleavage of metal σ-alkyls[3] and in the protonation of η^4-diene complexes to form η^3-allyl cations.[1] There are also cases where protonation leading to carbon–metal cleavage can be shown to take place directly on the organic ligand (i.e., σ-allyl to π-olefin).[4] There have been few detailed studies on the reactions of low oxidation state polynuclear organometallic complexes with protic acids.[5] The lower reactivity of the polynuclear organometallics holds out the possibility of observing intermediates in multistep protonation processes. Local differences in cluster atom environments and overall electrophilic reactivity of the ligand can be estimated from protonation studies followed by NMR.

Clusters of structural type $(H)Ru_3(CO)_9(C_2R)$ (I) are obtainable in good yields by reaction of $Ru_3(CO)_{12}$ with terminal acetylenes.[6] The dissolution of $Ru_3(CO)_{12}$ in 98% H_2SO_4 has



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