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Cyclopropylmethyl Derivatives of the Transition Metals. Insertion Reactions and Ring Openings with Formation of η^3-Crotyl and σ,π-Acyl Complexes Catalyzed by Triphenylphosphine

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Reactions of the salts $(\eta^5\text{-}C_5H_5)M(CO)_n^-Na^+$ (M = Fe, Mo, W; n = 2, 3) with cyclopropylmethyl bromide, CPM–Br, lead to good yields of the corresponding metal–CPM complexes. These undergo rapid CO insertion reactions upon treatment with PPh_3 in THF. The kinetics of the insertion reaction of the Mo complex have been performed, and it was shown to be 6 times faster than that of the Mo–methyl complex. The crystal structure of the related Fe complex is reported. Thermal treatment of the title complexes in hexane with PPh_3 leads to excellent yields of the ring opened and rearranged phosphine free η^3-crotyl complexes. In the specific case of the W complex, both the thermal and photochemical reactions lead to the formation of an extra complex, $(\eta^5\text{-}C_5H_5)\overline{W(CO)_2COCH_2CH_2CH}{=}CH_2$.

Introduction

There are few reported studies on cyclopropylmethyl derivatives of the transition metals.[1-4] The reaction of SO_2 with $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2$cyclopropyl, Fp–CPM, provides a rare example of SO_2 insertion into a C–C bond rather than into the Fe–C bond,[1] and during studies on the rearrangements of various homoallyl complexes, $MCH_2CH_2CH{=}CH_2$, to η^3-crotyl (1-methallyl) complexes, the complexes $(\eta^5\text{-}C_5H_5)M(CO)_n$–CPM (M = Fe, n = 2 ; M = Mo, n = 3) were briefly mentioned without any details of their analytical, spectral, or chemical properties.[2,3] Finally, San Fillipo used CPM–I as a substrate for the reactions of various metalate anions to ascertain the role of electron transfer in the reactions leading to metal–carbon bond formation.[4] This latter study takes advantage of the rapid rearrangement of the CPM radical to the butenyl radical.

As part of a study on the role of ion pairing in metal carbonylate reaction mechanisms, we had reason to synthesize some CPM complexes and wish to report on their thermal and photochemical reactivity in the presence, and absence, of triphenylphosphine. These reactions lead to a variety of complexes, some of which suggest that the rearrangements of the homoallyl complexes referred to above may conceivably occur via CPM intermediates.[2,3]

Results and Discussion

The thermal reactions of the CPM complexes are dependant upon the nature of the metal, the solvent, and the presence or absence of added triphenylphosphine.

Treatment of all three title complexes, $(\eta^5\text{-}C_5H_5)M(CO)_n$–CPM (M = Fe, Mo, W; n = 2, 3) with triphenylphosphine in THF leads to good yields of the corresponding CO insertion products $(\eta^5\text{-}C_5H_5)M(CO)_{n-1}(PPh_3)CO$–CPM. The X-ray crystal structure of the Fe complex is illustrated in Figure 1, and the various bonding parameters are recorded in Table III.

The various bond lengths and angles are generally unexceptional and coincide with those parameters known for the cyclopropane ring in other compounds, e.g. cyclopropanecarboxamide,[5] tricyanocyclopropane,[6] and other iron cyclopentadienylcarbonyl complexes.[7] The cyclopropyl group is eclipsed with the C=O group, C_4–C_3/C_1–O_2 torsion angle = 14.5°, with the ring pointed away from the ketone group. The terminal CO bond length is appropriately less than in related cyclopentadienyliron dicarbonyl complexes[7] due to the phosphine substitution.

A kinetic study was performed on the formation of the Mo complex and compared to the rate of insertion of the related Mo–methyl complex. The various kinetic data are recorded in Table IV, and it is clear that as with the methyl migration reaction the rate in THF is first order in Mo complex and independent of phosphine.[8] The rate of the CPM migration is 6 times faster than that of the methyl migration. This may be expected from a steric point of view where release of steric strain at the metal center enhances migration as demonstrated by the relative rates of migration previously published for this Mo system, Et > Me > Ph > $CH_2CH{=}CH_2$.[9] However, it is also clear that electron-withdrawing groups retard such alkyl migrations and the cyclopropyl group may be expected to retard such migrations. The relative importance of the two countering effects is difficult to assign, but the enhanced steric bulk seems to be most significant. This result will be valid irrespective of the exact mechanism of the insertion reaction. Recent studies have suggested the solvent plays an important role in insertion reactions, undertaking a nucleophilic attack upon the metal complex that promotes the alkyl migration.[10,11] The rate increase observed

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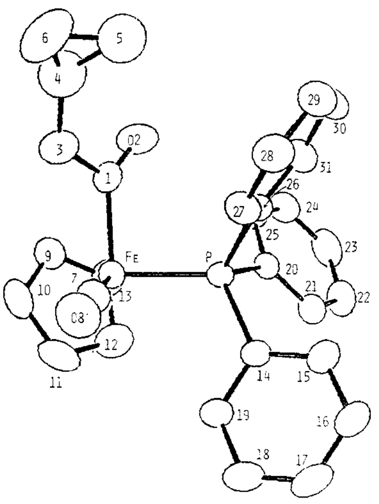


Figure 1.

with increasing steric bulk simply implies that the rate-determining step in this process involves considerable metal–carbon bond rupture.

In refluxing hexane, with no added ligand, infrared spectroscopic monitoring showed that the Fe and Mo complexes were slowly transformed to trace amounts of the corresponding η^3-crotyl complexes while the W complex showed no such reactivity. If the solvent is changed to decane in the case of the Fe complex, a reaction leading to the crotyl complex is complete within 4 h, but with much decomposition.

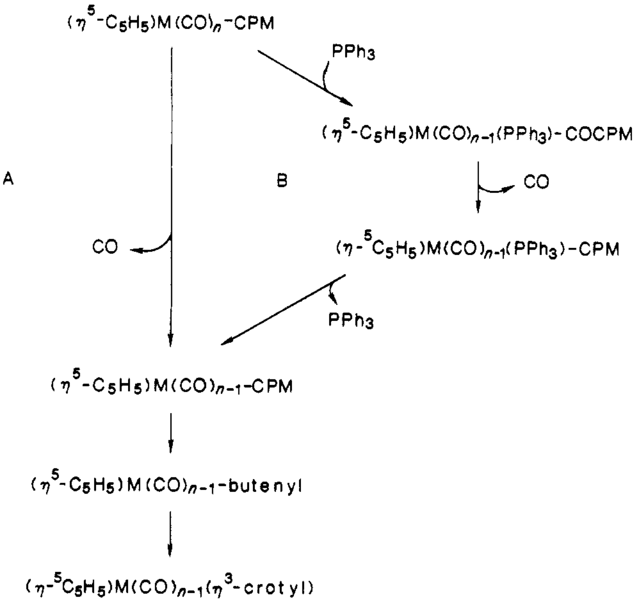
If triphenylphosphine is added to the reactions performed in refluxing hexane, a surprising result is obtained in the light of the above results. The complexes isolated from the Fe and Mo reactions are the η^3-crotyl complexes in high yield after 10–15 h; i.e., no phosphine-containing complexes were isolated. In the case of the Mo reaction it was possible to observe the transience of the CPM migration products described above, CPMCOMo, together with a trace amount of the corresponding decarbonylated product $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)CPM$. In reactions where the acyl complexes were treated either thermally or photochemically to attempt decarbonylations, to obtain the latter type of complex, only high yields of η^3-crotyl complexes were isolated. Furthermore, photochemical treatment of the starting Fe– and Mo–CPM complexes with PPh_3 also led to the formation and isolation of the η^3-crotyl complexes, along with the corresponding metal–metal bonded dimers. Again, no phosphine-containing complexes were obtained.

It is clear that in all experiments where we might have expected to form the phosphine-substituted CPM derivative $(\eta^5\text{-}C_5H_5)M(CO)_{n-1}(PPh_3)CPM$ (M = Fe, Mo), it was never obtained; only the η^3-crotyl complexes were isolated.

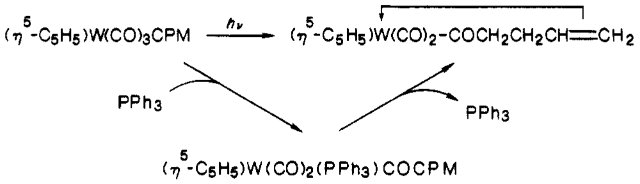
The above results suggest Scheme I may be applicable to the formation of the η^3-crotyl complexes, which were always formed as a mixture of syn and anti isomers as reported in the literature.[2,3,12]

In the absence of triphenylphosphine, pathway A is the only thermal route to the formation of the product. The slow nature of this reaction is due to the high energy needed for expulsion of the CO ligand to yield the needed intermediate 16e complex $(\eta^5\text{-}C_5H_5)M(CO)_{n-1}$–CPM. The mechanism for the rearrangement of the CPM unit to the crotyl system would involve cleavage of the M–C bond to yield the CPM radical followed by the rearrangement to butenyl radical and recombination. It has previously been established that such species readily rearrange to the η^3-crotyl complexes.[2,3] The formation of the 16e complex as the reactive species needed for metal–carbon bond cleavage, leading to unusual 15e intermediates, is in accord with several studies on the chemistry of Fe, Mo, W, and Mn alkyl complexes.[13-15]

Scheme I



Scheme II



In the presence of PPh_3, pathway B is operative. This involves rapid formation of the migration carbonyl insertion product, which in hexane will be a second-order reaction,[16] and is clearly faster than the dissociation of CO in route A. This complex then decarbonylates, and subsequent loss of phosphine leads to the same coordinatively unsaturated intermediate, $(\eta^5\text{-}C_5H_5)M(CO)_{n-1}$–CPM, needed for the final σ to π transformation. Clearly the two steps involved in the insertion/decarbonylation process occur much faster than the simple CO dissociation of pathway B. During the course of the reaction of the Mo complex, infrared monitoring indicated the transient formation of the acyl complex as well as a trace amount of the decarbonylated product.

Under photochemical conditions the reactions to yield the π-crotyl complexes proceed much faster in the absence of phosphine, pathway A, since now the loss of CO is more efficient.

For the W complex, such photochemical reactions did not lead to high yields of the crotyl complex but instead led to the phosphine substitution product $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CPM$, which is clearly more stable for the

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Table I. Spectral and Analytical Data for New Complexes

complex[c] (% yield)	IR data,[a] cm^{-1}	NMR data[b]		anal. found (calcd)	
		C_5H_5	CH_2cyclopropyl	C	H
1, $(\eta^5\text{-}C_5H_5)Mo(CO)_3CPM$ (80)	2018, 1935, 1901	5.3	1.75 (d, J = 6 Hz)	48.2 (48.1)	4.23 (4.03)
2, $(\eta^5\text{-}C_5H_5)W(CO)_3CPM$ ( )	2015, 1925, 1894	4.97	1.77 (d, J = 7 Hz)	37.2 (37.1)	3.17 (3.12)
3, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CPM$ (75)	2007, 1951	5.68	1.65 (d, J = 6.5 Hz)		
4, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)COCPM$ (50)	1934, 1851, 1622	4.9	2.8 (d, J = 7.5 Hz)	63.9 (64.0)	4.91 (4.84)
5, $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)COCPM$ (45)	1926, 1841, 1608	5.0	2.7 (d, J = 7 Hz)	55.8 (55.4)	4.29 (4.19)
6, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCPM$ (54)	1910, 1598	4.3 (d, J = 2)	2.96 (dd)	69.6 (70.4)	5.56 (5.50)
7, $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CPM$ (10)	1921, 1827			55.8 (55.9)	4.68 (4.37)
8, $(\eta^5\text{-}C_5H_5)\overline{W(CO)_2COCH_2CH_2CH}{=}CH_2$ (65)	1984, 1912, 1601	5.3	CH=CH 6.0 (m), 4.7 (m)	37.1 (37.1)	3.19 (3.12)

[a] Spectra recorded in CH_2Cl_2 except for the M–CPM complexes that were recorded in hexane. [b] All data in ppm recorded in $CDCl_3$; all cyclopropyl protons appear as a complex multiplet in the range 0.0–1.4 ppm. The aromatic protons are centered at 7.3 ppm. [c] Mass spectral data [complex, *m/e* (relative abundance)]: 1, 302 (2), 274 (18), 246 (40), 218 (100), 188 (50), 163 (60), 135 (33); **2**, 388 (12), 360 (8), 332 (15), 304 (100), 276 (40), 249 (40), 222 (15); **8**, 360 (40), 332 (10), 304 (100), 276 (40), 249 (20), 222 (15).

tungsten system, and/or the σ-acyl π complex $(\eta^5\text{-}C_5H_5)\overline{W(CO)_2\text{-}COCH_2CH_2CH}{=}CH_2$. Such complexes have been previously reported for the Fe system[17] and suggested as intermediates in the thermal decomposition of butenyl cobalt carbonyl complexes.[18] This is the first example of such a tungsten complex. This complex was formed not only from the photochemical treatment of the acyl complex but also by direct photochemical treatment of the starting CPM complex with and without addition of triphenylphosphine (Scheme II).

The inability of tungsten acyl complexes to readily decarbonylate, cf. Mo, has been previously observed[16] and is probably the cause of the differing chemistry noted in this study.

Mass spectral analysis of the title complex W–CPM exhibits a parent ion at *m/e* 388, and successive loss of carbon monoxide produces the ion that carries the majority of the ion current, *m/e* 304, which is presumably the W–η^3-crotyl complex. Three other ions at *m/e* 274, 247, and 222 are also observed. The W–η^3-crotyl and the W–$COCH_2CH_2CH{=}CH_2$ complexes both exhibit an identical mass spectrum, but the latter requires a much higher probe temperature before ions are observed. The spectrum is identical with that of the W–CPM complex with the exception that the parent ion in both cases is *m/e* 360. This behavior suggests that thermal decomposition is occurring in the mass spectrometer in which the σ,π-acyl complex transforms into the η^3-crotyl or CPM complex. Thermal treatment of the complex in hexane solution for prolonged periods of time did not effect this change.

The mass spectra of the Mo–CPM and π-crotyl complexes are essentially similar to those of the W complexes.

Experimental Section

All reactions were performed in inert atmospheres by using dry nitrogen or argon and dry, air-free solvents. Separations were performed by column chromatography using alumina on a 2.5 × 20 cm column.

Crystal Structure Determination (Data Collection and Analysis Parameters, Table II). A total of 4044 nonzero unique intensities were collected on a CAD-4 four-circle computer-controlled diffractometer using graphite-monochromated Mo K$^\alpha$ radiation (θ–2θ scan; θ limits $1.5 > \theta > 30.0°$, scan angle = $0.5 + 0.35 \tan \theta$). The size of the crystal used for data collection was 0.18 × 0.28 × 0.5 mm.

Atomic coordinates of the iron atom were obtained from Patterson synthesis (R = 0.46). The remaining non-hydrogen atoms were located in subsequent Fourier maps. A total of 2750 reflections ($I > 15\sigma(I)$) were used in isotropic least-squares refinement of the non-hydrogen atoms, and the hydrogen atoms were included in structure factor calculations in positions derived from assumed geometries. At the end of isotropic refinement (R = 0.104) an empirical absorption correction[19] was applied that dropped R to 0.068 (maximum, minimum, and average absorption corrections were 1.248, 0.377, and 1.00 respectively). Non-hydrogen atoms were further refined by anisotropic least squares using 3000 observations ($I > 1.7\sigma(I)$). The weighting scheme applied was $w = 4IL/\sigma(I)^2 + (0.01I^2)$, where I is the set intensity and L is the Lorenz–polarization factor.

Table II. Crystal Data, Data Collection, and Least-Squares Parameters

M_r	490.3
space group	$P2_1/n$
a, Å	15.864 (3)
b, Å	19.124 (3)
c, Å	7.958 (2)
β, deg	94.02 (2)
V, Å^3	2408.4 (1.5)
Z	4
D_{calcd}, g cm^{-3}	1.352
λ(Mo K$\bar{\alpha}$), Å	0.71073
μ(Mo K$\bar{\alpha}$), cm^{-1}	7.1
2θ limits, deg	3–60
scan technique	θ–2θ
max scan time, min	1.5
scan angle, deg	$0.5 + 0.35 \tan \theta$
total no. of intensities measd	5595
no. of reflctns with zero intensity	734
range of miller indices	
h	from 0 to 20
k	from 0 to 20
l	from −11 to 11
no. of reflctions used in least squares, N_o	3000 ($F_o \geq 1.7\sigma(F_o^2)$]
no. of variables, N_v	280
R	0.054
R_w	0.049
R_{tot}	0.118
$(\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v))^{1/2}$	1.883
empirical abs correctn (DIFABS)	
max correctn	1.248
min correctn	0.377
av correctn	1.000
crystal (brown)	
approx crystal size, mm	0.18 × 0.28 × 0.50

The final R values were R = 0.054, R_w = 0.049, and R_{tot} = 0.118, and $S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v)^{1/2}] = 1.88$, where N_o = number of observations (3000) and N_v = number of variables (280).

Synthesis of $(\eta^5\text{-}C_5H_5)M(CO)_n$–CPM (M = W; n = 3). To a cooled (0 °C) THF solution of $(\eta^5\text{-}C_5H_5)W(CO)_3^-Na^+$ prepared by standard techniques from 7.0 g (2.0 mmol) of $W(CO)_6$[20] was added a THF solution of a 10% excess of CPM–Br.[21] This mixture was allowed to warm to room temperature with stirring for 1 h and further stirred for 15 h. After filtration of NaBr, the solvent was removed under reduced pressure.

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Table III. Bond Lengths and Angles for Fe–CO–CPM

Bond Lengths (Å)

Fe–P	2.194 (1)	C(3)–C(4)	1.416 (7)	C(16)–C(17)	1.371 (6)
Fe–C(1)	1.956 (4)	C(4)–C(5)	1.420 (8)	C(17)–C(18)	1.375 (6)
Fe–C(7)	1.714 (4)	C(4)–C(6)	1.442 (8)	C(18)–C(19)	1.386 (6)
Fe–C(9)	2.116 (4)	C(5)–C(6)	1.490 (7)	C(20)–C(21)	1.384 (5)
Fe–C(10)	2.108 (4)	C(7)–O(8)	1.155 (5)	C(20)–C(25)	1.395 (5)
Fe–C(11)	2.124 (4)	C(9)–C(10)	1.395 (5)	C(21)–C(22)	1.397 (5)
Fe–C(12)	2.120 (4)	C(9)–C(13)	1.387 (5)	C(22)–C(23)	1.373 (6)
Fe–C(13)	2.113 (4)	C(10)–C(11)	1.421 (6)	C(23)–C(24)	1.367 (5)
P–C(14)	1.836 (4)	C(11)–C(12)	1.384 (6)	C(24)–C(25)	1.376 (5)
P–C(20)	1.826 (3)	C(12)–C(13)	1.423 (5)	C(26)–C(27)	1.386 (5)
P–C(26)	1.832 (4)	C(14)–C(15)	1.389 (5)	C(26)–C(31)	1.371 (5)
C(1)–O(2)	1.280 (4)	C(14)–C(19)	1.380 (5)	C(27)–C(28)	1.387 (5)
C(1)–C(3)	1.520 (5)	C(15)–C(16)	1.370 (6)	C(28)–C(29)	1.366 (6)
				C(29)–C(30)	1.360 (6)
				C(30)–C(31)	1.392 (6)

Bond Angles (deg)[a]

P–Fe–C(1)	90.9 (2)	C(4)–C(5)–C(6)	59.3 (6)
P–Fe–C(7)	91.8 (2)	C(4)–C(6)–C(5)	57.9 (6)
P–Fe–C(9)	136.7 (2)	Fe–C(7)–O(8)	176.7 (6)
P–Fe–C(10)	160.9 (2)	Fe–C(9)–C(10)	70.2 (4)
P–Fe–C(11)	123.4 (2)	Fe–C(9)–C(13)	70.7 (4)
P–Fe–C(12)	96.0 (2)	C(10)–C(9)–C(13)	109.1 (6)
P–Fe–C(13)	102.3 (2)	Fe–C(10)–C(9)	71.2 (4)
C(1)–Fe–C(7)	94.1 (3)	Fe–C(10)–C(11)	71.2 (4)
C(1)–Fe–C(9)	84.2 (2)	C(9)–C(10)–C(11)	107.2 (6)
C(1)–Fe–C(10)	105.2 (3)	Fe–C(11)–C(10)	69.6 (4)
C(1)–Fe–C(11)	144.4 (3)	Fe–C(11)–C(12)	70.8 (4)
C(1)–Fe–C(12)	140.9 (3)	C(10)–C(11)–C(12)	108.1 (6)
C(1)–Fe–C(13)	101.6 (3)	Fe–O(12)–C(11)	71.1 (4)
C(7)–Fe–C(9)	131.3 (3)	Fe–C(12)–C(13)	70.1 (4)
C(7)–Fe–C(10)	97.0 (3)	C(11)–C(12)–C(13)	108.0 (6)
C(7)–Fe–C(11)	94.0 (3)	Fe–C(13)–C(9)	71.0 (4)
C(7)–Fe–C(12)	124.0 (3)	Fe–C(13)–C(12)	70.6 (4)
C(7)–Fe–C(13)	158.6 (3)	C(9)–C(13)–C(12)	107.4 (6)
C(9)–Fe–C(10)	38.6 (3)	P–C(14)–C(15)	122.2 (5)
C(9)–Fe–C(11)	64.7 (3)	P–C(14)–C(19)	120.2 (5)
C(9)–Fe–C(12)	64.7 (3)	C(15)–C(14)–C(19)	117.6 (5)
C(9)–Fe–C(13)	38.3 (3)	C(14)–C(15)–C(16)	121.5 (6)
C(10)–Fe–C(11)	39.3 (3)	C(15)–C(16)–C(17)	119.9 (6)
C(10)–Fe–C(12)	65.1 (3)	C(16)–C(17)–C(18)	120.1 (7)
C(10)–Fe–C(13)	65.1 (3)	C(17)–C(18)–C(19)	119.6 (7)
C(11)–Fe–C(12)	38.1 (3)	C(14)–C(19)–C(18)	121.2 (6)
C(11)–Fe–C(13)	64.8 (3)	P–C(20)–C(21)	123.3 (5)
C(12)–Fe–C(13)	39.3 (3)	P–C(20)–C(25)	118.6 (4)
Fe–P–C(14)	115.1 (2)	C(21)–C(20)–C(25)	118.2 (5)
Fe–P–C(20)	115.6 (2)	C(20)–C(21)–C(22)	120.4 (6)
Fe–P–C(20)	117.0 (2)	C(21)–C(22)–C(23)	120.2 (6)
C(14)–P–C(20)	104.0 (3)	C(22)–C(23)–C(24)	119.8 (6)
C(14)–P–C(26)	100.0 (3)	C(23)–C(24)–C(25)	120.5 (6)
C(20)–P–C(26)	103.1 (3)	C(20)–C(25)–C(24)	120.9 (6)
Fe–C(1)–O(2)	123.1 (4)	P–C(26)–C(27)	117.6 (4)
Fe–C(1)–C(3)	118.3 (5)	P–C(26)–C(31)	124.3 (5)
O(2)–C(1)–C(3)	118.5 (6)	C(27)–C(26)–C(31)	118.1 (6)
C(1)–C(3)–C(4)	120.2 (7)	C(26)–C(27)–C(28)	120.9 (6)
C(3)–C(4)–C(5)	124.6 (8)	C(27)–C(28)–C(29)	120.0 (6)
C(3)–C(4)–C(6)	128.1 (8)	C(28)–C(29)–C(30)	119.8 (7)
C(5)–C(4)–C(6)	62.7 (7)	C(29)–C(30)–C(31)	120.5 (7)
		C(26)–C(31)–C(30)	120.7 (6)

[a] Esd's are given in parentheses.

Table IV. Kinetic Data for the Reaction Mo–CPM + PPh_3 in THF[a]

10^3[Mo–OPM], M	excess PPh_3	T, °C	k, mol^{-1}
1.57	10	30	4.36×10^{-2}
1.57	10	40	9.60×10^{-2}
1.85	10	50	2.21×10^{-1}
1.41	20	30	4.90×10^{-2}
1.41	30	30	4.84×10^{-2}
1.41	40	30	5.00×10^{-2}

[a] An experiment was performed on the rate of the related reaction between Mo–CH_3 and PPh_3 at 50 °C by using a 10-fold excess of the ligand, resulting in a rate constant of 3.9×10^{-2} m^{-1}.

To the residue was added 200 mL of a 60/40 hexane/methylene chloride mixture, and the solution was stirred for 2 h. Subsequent filtration and removal of solvent produced a crude product that was placed on an alumina column in an 80/20 hexane/methylene chloride mixture and eluted with the same solvent mixture, resulting in a yellow band of the title product. Recrystallization from hexane led to a 70% yield. The infrared, mass, NMR spectral, and analytical data for the complex are recorded in Table I.

Similar reactions involving the corresponding Fe and Mo anions led to similar yields of the related metal–CPM complexes, whose spectral data are also included in Table I.

Thermal Treatment of M–CPM Complexes with PPh_3 in THF (M = Mo). A mixture of 0.3 g (1.0 mmol) of the title complex and a 50% excess of PPh_3 was refluxed in THF (60 mL) for 40 min. At this time there was no evidence for any remaining starting material. The solvent was removed under vacuum and the product extracted with a methylene chloride/hexane (40/60) mixture. The mixture was placed upon an alumina column and eluted initially with hexane to remove a pale yellow band of starting materials. Subsequent elution with a 40/60 methylene chloride/hexane solvent mixture produced a orange band that was collected and recrystallized from hexane/methylene chloride to produce a 60% yield of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)$COCPM. Analytical and spectral data are recorded in Table I.

The related Fe and W complexes were formed in similar yields in the same fashion, and their analytical and spectral data are also recorded in Table I.

Thermal Treatment of M–CPM Complexes in Hexane (M = Fe). A solution of 0.5 g (2.1 mmol) of the iron complex was refluxed in hexane and monitored by infrared spectroscopy. After 24 h small amounts of the η^3-crotyl complex were observed. When the reaction was left for 16 days, almost complete loss of starting material was observed, with significant decomposition, and modest amounts of the η^3-crotyl complex. If the same reaction was performed in decane, conversion was complete within 4 h, but with similar decomposition.

Similar reactions with the Mo– and W–CPM complexes gave small amounts of the Mo–crotyl complex formation, but no evidence for the transformation of the W complex.

Thermal Treatment of M–CPM Complexes in Hexane with PPh_3 (M = Mo). A mixture of 0.3 g (1.0 mmol) of the title complex and 0.7 g (2.6 mmol) of PPh_3 was refluxed in hexane. After 14 h, infrared spectroscopic monitoring indicated that 80% of the starting material was absent and that the major products in solution were the carbonyl insertion product Mo–CO–CPM and the η^3-crotyl complex. Small amounts of a complex with CO stretching frequencies at 1946 and 1892 cm^{-1} were also observed. We suggest that this complex is $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)$CPM, but it was not possible to obtain the material in high enough yield for characterization. The reaction was permitted to continue for 36 h at which time the only complex present in solution appeared to be the η^3-crotyl complex. The solvent was removed under vacuum and the yellow product purified by column chromatography (alumina), eluting with hexane containing 5% methylene chloride. Recrystallization from hexane resulted in a 40% yield of the η^3-crotyl complex, characterized by the equivalence of its spectral properties with those published.[3,12]

A similar reaction with the Fe–CPM complex, without monitoring, provided 38% yield of the iron η^3-crotyl complex. With the W–CPM complex, no reaction was apparent after 15 h.

Photochemical Treatment of M–CPM with PPh_3 (M = W). In a quartz tube 1.5 g (3.8 mmol) of $(\eta^5\text{-}C_5H_5)W(CO)_3$CPM was added to 1.2 g (4.5 mmol) of triphenylphosphine in 150 mL of hexane. The solution was irradiated with a low-pressure mercury lamp and the reaction monitored by infrared spectroscopy. After 18 h most of the starting material had been consumed, and the irradiation was stopped. The solution was filtered and the hexane solution concentrated to 50 mL and placed in a refrigerator to yield 0.9 g (60%) of yellow crystalline $(\eta^5\text{-}C_5H_5)W(CO)_2COCH_2CH_2CH{=}CH_2$, mp 101–102 °C.

The filtrate from the above recrystallization was placed upon an alumina column and eluted with hexane to produce a yellow and a red band. The yellow band was eluted with hexane to yield a mixture of starting material and triphenylphosphine. The red-brown band was eluted with a hexane/methylene chloride

(60/40) solution, and subsequent recrystallization from the same solvent yielded 0.2 g (10%) of $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)$CPM, mp 135–137 °C.

Kinetic Analysis. Kinetic studies on the rate of the reaction between Mo–CPM and PPh_3 were performed in THF under pseudo-first-order conditions, monitoring the rate of disappearance of the CO stretching frequency at 2012 cm^{-1}. All spectroscopic analysis was performed by using a Perkin-Elmer 580B infrared instrument and CaF_2 cells. The reaction was found to be first order with respect to the Mo complex and zero order with respect to PPh_3. The various rate constants are recorded in Table IV, and the resulting activation parameters are $\Delta H = 11.2$ kcal/mol and $\Delta S = -28.0$ eu.

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Supplementary Material Available: Tables of atomic coordinates, temperature factor expressions, and complete bond lengths and bond angles for the Fe–COCPM structure (6 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Chemistry of $(RC_5H_4)_2TiS_5$. New Information on Its Reactions with Nucleophiles, Syntheses and Reactions of 1,4-$[(RC_5H_4)_2Ti]_2S_4$, and a Second Isomer of $(RC_5H_4)_2TiS_2C_2(CO_2Me)_2$

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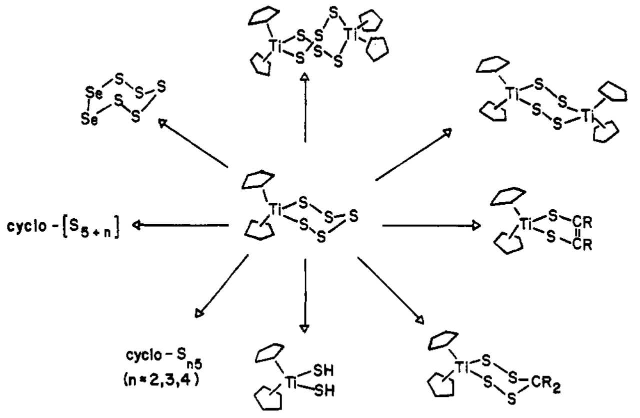
Described are a series of reactions of $[(RC_5H_4)_2TiS_x]_n$ (R = H, CH_3, *i*-Pr; $x = 5$ (**1**, $n = 1$), 3 (**2**, $n = 2$), 2 (**3**, $n = 2$)). The reactions of **1** with organophosphines in the presence of acetylenes gives the dithiolenes $(RC_5H_4)_2TiS_2C_2R_2$. In the absence of acetylenes desulfurization of **1** gives the dimers $[(RC_5H_4)_2Ti]_2S_x$ (x = 4, 6). These dimers could not be prepared from $(RC_5H_4)_2TiCl_2$ and Li_2S_x; however, reaction of $(RC_5H_4)_2TiCl_2$ and Li_2S_2 in the presence of CS_2 gives high yields of **3**. The oxidation of $(RC_5H_4)_2Ti(SH)_2$ also gives **3**. The mechanisms of these reactions are discussed in light of corresponding work on 1,2-$C_6H_4(SR)_2$ (R = H, S_x). The structure of 1,4-$[(i\text{-}PrC_5H_4)_2Ti]_2S_4$ (**3c**) was determined by X-ray crystallography. It crystallizes in the monoclinic space group $C2/c$ with $a = 35.481$ (10) Å, $b = 10.976$ (3) Å, $c = 23.553$ (6) Å, $\beta = 130.74$ (3)°, $V = 6950$ (3) Å^3, and $Z = 4$ and refined to $R = 0.052$ and $R(w) = 0.074$. The analysis confirms the structure as an 1,4-M_2S_4 ring in the chair conformation. Whereas **1** reacts with electrophilic acetylenes to give dithiolenes, the corresponding ambient temperature reaction of **3** with dialkyl acetylenedicarboxylates (DEAD or DMAD) gives vinyl disulfides. The structure of the vinyl disulfide complex $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_2CH_3)_2$ (**4**) was confirmed by X-ray diffraction (monoclinic, $P2_1/n$; $a = 9.772$ (2) Å, $b = 14.573$ (2) Å, $c = 11.756$ (2) Å, $\beta = 100.25$ (1)°, $V = 1647.4$ (5) Å^3, and $Z = 4$; refinement to R = 0.0387 and $R(w) = 0.0411$). The TiSSCC ring adopts an envelope conformation. The formation of **4** from **3** occurs via a bimolecular pathway according to the following equation $d[4]/dt = (4.2 \times 10^{-3}\ M^{-1}\ s^{-1})[3][DMAD]$. Compound **4** easily rearranges to give the dithiolene. Labeling studies (C_5H_5 vs. $CH_3C_5H_4$; DMAD vs. DEAD; ^{32}S vs. ^{34}S) demonstrate the intramolecularity of this rearrangement. These findings suggest that other acetylene–metal sulfide reactions may proceed via this unexpected pathway.

Introduction

There is presently great interest in the coordination chemistry of main-group atoms, chains, and clusters. Considerable information is already available concerning the structural chemistry of transition metal derivatives of "naked" metalloids. Relatively little is however known about the *reactivity* of these simple main-group ligands.

In recent years our interests have focused on inorganic sulfur ligands. Molecular metal sulfides, disulfides, and polysulfides are well-known. Binary metal sulfido anions and the neutral metal carbonyl and cyclopentadienyl sulfides have received the greatest attention. The metal sulfido anions are attractive because of their relative simplicity, and studies on such compounds are relevant to important transformations underlying various industrial,[1] biological,[2] and mineralogical[3] processes. The organometallic sulfides are of special interest because, in our opinion, their reaction chemistry presently exceeds in scope

Scheme I



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