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PHOTOCHEMICAL REACTIONS OF CYCLOHEPTATRIENETRICARBONYLCHROMIUM

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SUMMARY

The preparations of $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ by the photochemical reaction of cycloheptatrienetricarbonylchromium with triphenylphosphine or triphenyl phosphite are described. The mass spectra of the compounds are compared with those of $C_7H_8Cr(CO)_3$ and $C_6H_6Cr(CO)_2P(C_6H_5)_3$. Attempts to prepare compounds of the type $X_3Cr(CO)_2P(C_6H_5)_3$ and $X_3Cr(CO)_2P(OC_6H_5)_3$ by thermal reaction of $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ with benzonitrile, acetonitrile, or pentamethyldiethylenetriamine are discussed.

INTRODUCTION

The thermal reaction of cycloheptatrienetricarbonylchromium with nitriles[1] or isocyanides[2] produces compounds of the type *fac*-$X_3Cr(CO)_3$. Reaction of cycloheptatrienetricarbonylmolybdenum with nitrogen or phosphorous donor ligands also produces the derivatives *fac*-$X_3Mo(CO)_3$[3]. However, only one compound of the type $C_7H_8M(CO)_2L$ (M = Mo, Cr), in which a carbonyl group has been replaced rather than the cycloheptatriene ring, has been reported[4].

Photochemical reactions of arene–chromium tricarbonyls with nitrogen, phosphorus, sulfur, or olefinic ligands to give $ArCr(CO)_2L$ are well-known[5–7]. We wish to report the photochemical synthesis of $C_7H_8Cr(CO)_2L$, [$L = P(C_6H_5)_3$ or $P(OC_6H_5)_3$].

EXPERIMENTAL

All syntheses and isolations were carried out under a nitrogen atmosphere. Purification of the derivatives was performed in an inert atmosphere box. Infrared spectra were measured as Nujol mulls on Perkin–Elmer model 180 or 337 spectrophotometers using sodium chloride plates. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany. Mass spectra were obtained with a DuPont (CEC) 21-110B mass spectrometer. The samples were introduced in the direct insertion probe at a block temperature of 100 to 135°.

Cycloheptatrienetricarbonylchromium (Strem) was purified by subliming out any $Cr(CO)_6$ present and then recrystallizing from heptane. Tetrahydrofuran (Fisher) was refluxed for 24 h over potassium, distilled, and stored over sodium. Triphenylphosphine (Beacon) was recrystallized from methanol. Triphenyl phosphite (Aldrich), benzonitrile (Aldrich), pyridine (Baker), cyclooctene (Matheson, Coleman and Bell), acetonitrile (Baker), and pentamethyldiethylenetriamine (K and K) were used without further purification.

Photochemical reactions were carried out in a 250 ml, three-neck, round bottom flask equipped with an overhead stirrer. The flask was surrounded by dry ice in a Dewar vessel. The reaction mixture was irradiated with a 100 W, long-wavelength (3660 Å), ultraviolet lamp.

(*a*). *Cycloheptatrienedicarbonyl(triphenylphosphine)chromium*

A 0.5 g sample of $C_7H_8Cr(CO)_3$ (2.2 mmoles) was dissolved in 45 ml THF and the solution cooled while flushing with nitrogen. Triphenylphosphine (0.63 g; 2.4 mmoles) was added and the solution irradiated for 46 h after which time little starting material remained (as evidenced by the CO stretching vibrations in the IR).

The volume of solution was reduced *in vacuo* and cold (−78°) heptane added. Further reduction in volume yielded a dark reddish-brown solid. The crude product was washed with several small portions of hexane to remove $C_7H_8Cr(CO)_3$ and then dissolved in a minimum amount of dioxane. After filtration, the volume was reduced and the red solid precipitated by addition of hexane. (Found: C, 69.89; H, 5.12; P, 6.47. $C_{27}H_{23}O_2PCr$ calcd.: C, 70.13; H, 5.01; P, 6.70%.) Yield 35%; m.p. 55° (dec.); ν(CO) 1818, 1902 cm^{-1} (P–E 180).

(*b*). *Cycloheptatrienedicarbonyl(triphenyl phosphite)chromium*

$C_7H_8Cr(CO)_3$ (0.44 g; 1.9 mmoles) was dissolved in 40 ml THF, 0.90 g of triphenyl phosphite (2.9 mmoles) added, and the solution irradiated as above. Reaction was essentially complete after 48 h. Purification of $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ was accomplished in a manner similar to that for the phosphine derivative except that THF was used in place of dioxane. Some $C_7H_8Cr(CO)[P(OC_6H_5)_3]_2$, evidenced by a carbonyl band at 1830 cm^{-1} in the IR spectrum, appeared to be formed in the reaction in addition to the monosubstituted derivative. Characterization of the disubstituted derivative was not attempted. (Found: C, 63.70; H, 4.47; P, 5.90. $C_{27}H_{23}O_5PCr$ calcd.: C, 63.53; H, 4.54; P, 6.07%.) Yield 39%; m.p. 115° (dec.); ν(CO) 1834, 1916 cm^{-1} (P–E 180); NMR (τ, ppm in $CDCl_3$): 4.67 (broad multiplet), 5.53 (broad multiplet), 7.24 (doublet), 8.52.

(*c*). *Attempted photochemical reactions of cycloheptatrienetricarbonylchromium with pyridine, benzonitrile, and cyclooctene*

The solutions of $C_7H_8Cr(CO)_3$ and the desired ligand in a 1/1 mole ratio were irradiated as above. When pyridine was used as the ligand, a dark solid possessing carbonyl stretching vibrations at 1790 and 1870 cm^{-1} (P–E 337) was obtained from the deep violet reaction mixture. Purification of the solid, which appears to be $C_7H_8Cr(CO)_2Py$, was not accomplished, due to extreme air sensitivity. No IR bands indicative of carbonyl substitution were observed when benzonitrile and cyclooctene were used as ligands.

(d). Thermal reactions of cycloheptatrienetricarbonylchromium with pentamethyldiethylenetriamine (PEMdien), benzonitrile and acetonitrile

$C_7H_8Cr(CO)_3$ (2 mmole) was stirred with the neat amine or nitrile under a nitrogen atmosphere. (PEMdien)$Cr(CO)_3$ and $(C_6H_5CN)_3Cr(CO)_3$ were formed in a few minutes at room temperature. $(CH_3CN)_3Cr(CO)_3$ was formed by heating for two hours at 80–90°. The products were identified by comparison of their IR spectra with those reported in the literature for $(RCN)_3Cr(CO)_3$[1] and (PEMdien)$Mo(CO)_3$[8].

(e). Attempted thermal reactions of cycloheptatrienedicarbonyl(triphenylphosphine)-chromium and cycloheptatrienedicarbonyl(triphenyl phosphite)chromium with acetonitrile, benzonitrile, and PEMdien

$C_7H_8Cr(CO)_2P(C_6H_5)_3$ (0.5–1.0 mmole) or $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ was stirred with neat acetonitrile, benzonitrile, or PEMdien at room temperature for several hours. No substitution for the cycloheptatriene ring occurred, and no decrease in the intensities of the IR bands for $C_7H_8Cr(CO)_2L$ was observed. At 80–100° decomposition of the dicarbonyl compound occurred, but no product of the type $X_3Cr(CO)_2P(C_6H_5)_3$ or $X_3Cr(CO)_2P(OC_6H_5)_3$ was formed.

DISCUSSION

The compounds $C_7H_8Cr(CO)P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ are air-sensitive, crystalline solids which are slightly soluble in aliphatic hydrocarbons and moderately soluble in aromatic solvents, acetone, and chloroform. Solutions of these compounds decompose more readily in air than do the pure solid compounds.

The inability to isolate $C_7H_8Cr_2(CO)_2Py$ is consistent with the lower stability of the Py derivative of $ArCr(CO)_3$ compared with phosphine and phosphite derivatives[9]. The inability to form $C_7H_8Cr(CO)_2$(cyclooctene) may be either a result of the particular olefin used or a reflection of the donor–acceptor character of the cycloheptatriene ring[10].

The NMR spectrum of $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ in $CDCl_3$ showed broad cycloheptatriene ring proton peaks at τ 4.67, 5.53, 7.24 (doublet), and 8.52 ppm having relative areas 2/2/3/1 in good agreement with the spectrum of $C_7H_8Cr(CO)_3$ (multiplets centered at τ 4.0, 5.2, 6.7 and 8.2 ppm). The spectrum of the dicarbonyl derivative is less complex than that of the tricarbonyl and the peaks are all shifted to higher field. The high field shift of the ring protons has been observed previously for $C_5H_5Mn(CO)_2(NCC_6H_5)$[11] and $[1,4\text{-}(CH_3OOC)_2C_6H_4]Cr(CO)_2L$[12] in comparison with the corresponding tricarbonyl compounds. Although the shift in the position of the ring protons does not seem to be related in a simple fashion to electronic effects in molecules of this type[12,13], the upfield shift is consistent with increased electron density on the cycloheptratiene ring as a result of substitution of $P(OC_6H_5)_3$ for CO. This could arise either from a decrease in ring to metal bonding or an increase in metal to ring backbonding upon carbonyl substitution.

Mass spectral results for $C_7H_8Cr(CO)_2L$ [$L = CO$, $P(C_6H_5)_3$, $P(OC_6H_5)_3$] and $C_6H_6Cr(CO)_2L$ [$L = P(C_6H_5)_3$] are listed in Table 1. The spectrum of $C_7H_8Cr(CO)_3$ is similar to those reported previously[14,15]. The relatively large differences in intensities of the $C_7H_8^+$ and $C_7H_7^+$ peaks among the three spectra suggest that some thermal decomposition of the compound occurs in the mass spectrometer. Somewhat

TABLE 1

RELATIVE INTENSITIES OF IMPORTANT FRAGMENTS IN THE MASS SPECTRA OF $C_7H_8Cr(CO)_2L$ [L=CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$] AND $C_6H_6Cr(CO)_2P(C_6H_5)_3$

Fragment	*$C_7H_8Cr(CO)_2L$*					*$C_6H_6Cr(CO)_2P(C_6H_5)_3$*	
	L=CO[a]	*L=CO*[b]	*L=CO*	*L=$P(C_6H_5)_3$*	*L=$P(OC_6H_5)_3$*	*Fragment*	*Rel. int.*
$C_7H_8Cr(CO)_2L^+$	29	19	31	11	9.6	$C_6H_6Cr(CO)_2P(C_6H_5)_3^+$	15
$C_7H_8Cr(CO)L^+$	17	5.4	4.6	~0	<0.5	$C_6H_6Cr(CO)P(C_6H_5)_3^+$	~0
$C_7H_8CrL^+$	22	12	19	51	65	$C_6H_6CrP(C_6H_5)_3^+$	53
$C_7H_8Cr^+$	104	58	107	<5	⩽2	$C_6H_6Cr^+$	≤3
$Cr\text{-}L^+$		2.6	8.2	99	100	$Cr\text{-}P(C_6H_5)_3^+$	143
Cr^+	100	100	100	100	100	Cr^+	100
$C_7H_8^+$	97		8.5	31	370	$C_6H_6^+$	69
$C_7H_7^+$	104	9.0	34	98	140	$C_6H_5^+$	15
L^+			17	450	615	$P(C_6H_5)_3^+$	131
$P(C_6H_4)_2^+$				356		$P(C_6H_4)_2^+$	83
$PC_6H_5^+$				114		$PC_6H_5^+$	40
$OP(OC_6H_5)_3^+$					106		
$P(OC_6H_5)_2^+$					1370		

[a] Ref. 14. [b] Ref. 15.

less decomposition occurs in our experiments than in those of King[14], but somewhat more than in those of Müller and Fenderl[15].

The mass spectra of $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ are consistent with a structure in which one CO group of $C_6H_8Cr(CO)_3$ is replaced by $P(C_6H_5)_3$ or $P(OC_6H_5)_3$ and are similar to that of $C_6H_6Cr(CO)_2P(C_6H_5)_3$. The high intensities of the $P(C_6H_5)_3^+$ and $P(OC_6H_5)_3^+$ peaks may arise from both thermal decomposition of the compounds and from unreacted starting material present in the sample. The relative intensities of the ions containing phosphorus but no Cr are similar to the intensities of these ions in the spectra of $P(C_6H_5)_3$ and $P(OC_6H_5)_3$.

On the basis of percentage of total ion current for Cr containing ions, the relative stabilities of $C_7H_8Cr(CO)_2L^+$ and $C_6H_6Cr(CO)_2P(C_6H_5)_3^+$ are less than those of $C_7H_8Cr(CO)_3^+$ and $C_6H_6Cr(CO)_3^+$ respectively. These results parallel the relative thermal stabilities of the molecules and are in agreement with those reported previously for the compounds $C_5H_5Mn(CO)_2L$[16,17] [L = PR_3, $P(OR)_3$, olefin], and $C_4H_4NMn(CO)_2L$[18] [L = CO, $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$].

In contrast to the stepwise loss of carbonyl groups which is observed for C_7H_8-$Cr(CO)_3^+$, both CO groups appear to be lost simultaneously from $C_7H_8Cr(CO)_2L^+$. This is consistent with results for $C_5H_5Mn(CO)_2L^+$ [16,17] and $C_4H_4NMn(CO)_2L^+$ [18] and suggests that the presence of the L group weakens the M–CO bonds. The much larger abundance of $C_7H_8CrL^+$, and CrL^+ in the spectra of the dicarbonyl compounds than $C_7H_8Cr{-}CO^+$ and $Cr{-}CO^+$ in the tricarbonyl spectrum suggests that the $Cr{-}L^+$ bond is stronger than the $Cr{-}CO^+$ bond. Furthermore, the intensity of the $Cr{-}L^+$ peak is much greater than that of the $C_7H_8Cr^+$ peak in $C_7H_8Cr(CO)_2L$. This observation suggests that the $Cr{-}L^+$ bond is also stronger than the $C_7H_8{-}Cr^+$ bond. These data are in striking contrast to the results for $C_5H_5Mn(CO)_2L$[16,17] in which the $C_5H_5{-}Mn^+$ peak intensity is much greater than the $Mn{-}L^+$ peak intensity.

Attempted reactions of $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(O$-$C_6H_5)_3$ with acetonitrile, benzonitrile, and pentamethyldiethylenetriamine failed to produce the expected $X_3Cr(CO)_2L$ derivatives. On the other hand, $C_7H_8Cr(CO)_3$ reacted smoothly with benzonitrile or pentamethyldiethylenetriamine at room temperature and with acetonitrile at 80–90° to produce the compounds $X_3Cr(CO)_3$ (X = acetonitrile, benzonitrile, pentamethyldiethylenetriamine). These results suggest that the strengths of the chromium–cycloheptatriene bonds are increased by substitution of $P(C_6H_5)_3$ or $P(OC_6H_5)_3$ for a carbonyl group in the complex. This implies that the observed upfield shifts in the NMR of the ring protons are a result of increased backbonding from the metal to the ring when CO is replaced by $P(OC_6H_5)_3$ or $P(C_6H_5)_3$ (*vide supra*). Also, the decreased thermal stabilities of $C_7H_8Cr(CO)_2L$ as compared to $C_7H_8Cr(CO)_3$ are most likely a result of increased tendency of the dicarbonyl compounds to lose carbonyl groups rather than an increased tendency to lose the cycloheptatriene ring. This is in agreement with the mass spectral data.

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