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STRUCTURAL AND CATALYTIC ACTIVITY STUDIES ON PHOSPHINE— AND PHOSPHITE—DICARBONYLCHROMIUM COMPLEXES OF PHENANTHRENE AND NAPHTHALENE

MICHAEL CAIS *, M. KAFTORY, D.H. KOHN and D. TATARSKY

Department of Chemistry, Technion-Israel Institute of Technology, Haifa (Israel)

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Summary

The syntheses of phenanthrene$Cr(CO)_2L$ ($L = PEt_3$, PBu_3, PPh_3, $SbPh_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OBu)_3$ and $P(OPh)_3$) and naphthalene$Cr(CO)_2L$ ($L = PEt_3$, PBu_3, PPh_3 and $P(OPh)_3$) are reported. The behaviour of these complexes as catalysts for hydrogenation of dienes is described and X-ray structural features of two complexes, phenanthrene$Cr(CO)_2PEt_3$ and naphthalene$Cr(CO)_2P(OPh)_3$ are discussed in relation to their behaviour in catalytic reactions. It is suggested that stereoelectronic factors determine the catalytic properties of these complexes.

Introduction

In an accompanying paper [1] we discussed the significant changes which occur in the catalytic properties of arene$Cr(CO)_3$ complexes following the replacement of a CO group by other ligands to give complexes of the type arene$Cr(CO)_2L$ ($L = CS$, $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $P(OC_6H_5)_3$, PF_3, $CNCH_2C_6H_5$, $CNC(O)C_6H_5$, $CNC(O)N(CH_3)_2$). In all those complexes the arene moieties were substituted benzenes in which the substituents were either electron-withdrawing (CO_2Me, $C(O)CH_3$) or electron-releasing (CH_3, OCH_3) groups.

The effect of such groups upon the catalytic properties of substituted-benzenes $Cr(CO)_3$ complexes in the hydrogenation of dienes has been documented [2]. The hydrogenation conditions employed were relatively drastic, with temperatures usually around 150—160°C and hydrogen pressures of about 50 atm. It was subsequently found that with polycyclic arenes, the tricarbonylchromium complexes in coordinating solvents could catalyze the hydrogenation reaction under much milder conditions, such as 40°C and 4 atm with phenanthrene$Cr(CO)_3$ [3,4] and ambient temperatures and pressures with naphthalene$Cr(CO)_3$ [5,6]. A possible connection between features of the tricarbonylchromium complexes of phenanthrene and naphthalene, as observed from X-ray structural studies [7], and the special catalytic activity of these complexes has been suggested [3]. In view of the rather disappointing, though instructive, catalysis results, obtained with substituted-benzenes$Cr(CO)_2L$ complexes [1] and, on the other hand, knowing the special catalytic properties of tricarbonylchromium polycyclic arene complexes it appeared of interest to us to prepare phenanthrene$Cr(CO)_2L$ and naphthalene$Cr(CO)_2L$ complexes and study their bonding features and catalytic properties. In this communication we present data for several such complexes with $L = PR_3$ and $L = P(OR)_3$.

Results and discussion

The photosubstitution of arenechromium tricarbonyl complexes [7] was used to prepare the phosphine and phosphite derivatives of phenanthrene$Cr(CO)_2L$ and naphthalene$Cr(CO)_2L$ shown in Table 1. As can be seen from the data in Table 1, the replacement of a CO group by a phosphine or phosphite ligand produces a significant lowering of the IR frequency of the remaining carbonyls ($\Delta\nu(CO) \simeq 50$—$80\ cm^{-1}$) similar to that observed with the analogous benzene derivatives [1,7]. The differences between the various phosphorylated ligands in their donor-acceptor properties, as deduced from the variance of their effect on the lowering of the IR frequency of the remaining carbonyls, are maintained in the phenanthrene and naphthalene derivatives. The same ordering of these ligands as a function of increasing donor properties ($P(OR)_3 < P(Aryl)_3 < P(Alkyl)_3$) is observed as that in the complexes of the benzene series [1,7]. This result was of particular interest to us because it indicated the possibility that the overall bonding interactions in the arene-metal part of the complex, might

TABLE 1

PHENANTHRENE$Cr(CO)_2L$ AND NAPHTHALENE$Cr(CO)_2L$ COMPLEXES AND THEIR $\nu(CO)$-IR FREQUENCIES

Ligand L	Phenanthrene (CO) (cm^{-1})		Naphthalene (CO) cm^{-1}	
	Cyclohexane	THF	Cyclohexane	THF
CO	1980, 1912, 1902	1960, 1885	1980, 1920, 1905	1960, 1880
PEt_3	1895, 1845 [a]	1880, 1825 [a]	1880, 1830	
PBu_3	1900, 1850 [b]	1885, 1835 [b]	1900, 1845 [c]	1890, 1825 [c]
PPh_3	1911, 1862 [d]	1895, 1845 [d]	1908, 1852 [e]	1890, 1835 [e]
$SbPh_3$	1905, 1860	1890, 1840		
$P(OMe)_3$	1913, 1869 [f]	1900, 1850 [f]		
$P(OEt)_3$	1912, 1872 [g]	1900, 1845 [g]		
$P(OBu)_3$	1912, 1865	1895, 1840		
$P(OPh)_3$	1925, 1880 [h]	1915, 1860 [h]	1920, 1875 [i]	1912, 1860 [i]

[a] Calcd. for $C_{22}H_{25}CrO_2P$: C, 58.40; H, 5.53; P, 6.86%; m.wt., 404.0997. Found: C, 58.49; H, 5.60; P, 7.14%; M^+, 404.0761. [b] Calcd. for $C_{28}H_{37}CrO_2P$: m.wt., 488.19. Found: M^+, 488. [c] Calcd. for $C_{24}H_{35}CrO_2P$: m.wt., 438.18. Found: M^+, 438. [d] Calcd. for $C_{34}H_{25}CrO_2P$: C, 74.45; H, 4.56; P, 5.65%; m.wt., 548.1207. Found: C, 73.91; H, 4.67; P, 6.35%; M^+, 548.1698. [e] Calcd. for $C_{30}H_{23}CrO_2P$: m.wt., 498.08. Found: M^+, 498. [f] Calcd. for $C_{19}H_{19}CrO_5P$: m.wt., 410.04. Found: M^+, 410. [g] Calcd. for $C_{22}H_{25}CrO_5P$: m.wt., 452.08. Found: M^+, 452. [h] Calcd. for $C_{34}H_{25}CrO_5P$: C, 68.45; H, 4.19; P, 5.20%; m.wt., 596.0844. Found: C, 68.33; H, 4.32; P, 5.74%; M^+, 596.0806. [i] Calcd. for $C_{30}H_{23}CrO_5P$: m.wt., 546.0688. Found: M^+, 546.0551.

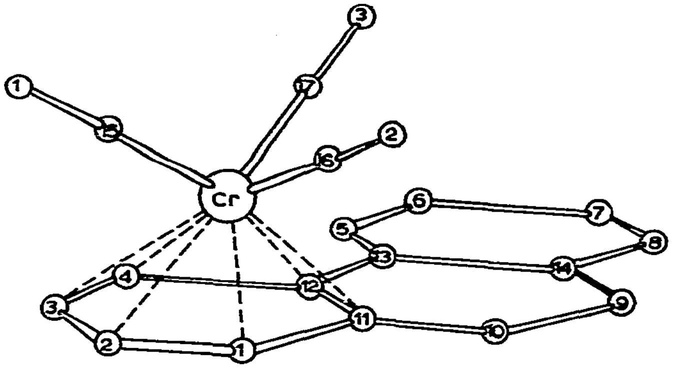


Fig. 1.

Bond between atoms	PhenCr(CO)$_3$(Å) [a]	PhenCr(CO)$_2$PEt$_3$(Å)
Cr—C(1)	2.212	2.166
Cr—C(2)	2.210	2.175
Cr—C(3)	2.206	2.199
Cr—C(4)	2.208	2.222
Cr—C(12)	2.289	2.322
Cr—C(11)	2.289	2.288
Cr—C(15)	1.828	1.813
Cr—C(16)	1.844	1.820
Cr—X(17)	1.857	2.323
C(15)—O(1)	1.145	1.163
C(16)—O(2)	1.165	1.166
X(17)—O(3)	1.136	

[a] Data taken from Ref. 10.

Fig. 1. Partial molecular diagram and bond distances for phenanthreneCr(CO)$_2$P(C$_2$H$_5$)$_3$.

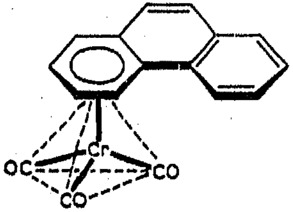
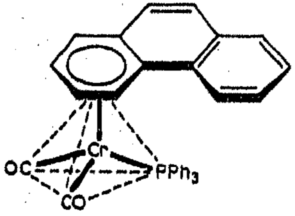
not undergo significant changes in the phenanthrene and naphthalene complexes, upon replacement of a carbonyl group by a phosphorylated ligand. As already mentioned, and as will be further discussed below, the special bonding features in the tricarbonylchromium complexes of phenanthrene and naphthalene, as revealed by X-ray studies, have been considered to be one of the factors responsible for the good catalytic properties of these complexes in the hydrogenation of dienes [3]. It seemed desirable to determine by X-ray studies if similar arene—metal bonding features were also present in the phosphorylated complexes of phenanthrene and naphthalene. Furthermore, it was hoped that the X-ray studies would also provide information on steric aspects of the phosphorus ligands in view of a reported dominant role of steric effects of such ligands in Ni^0 and other metal complexes [8].

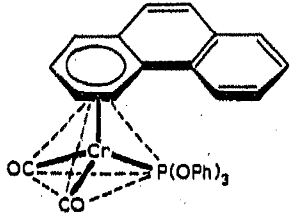
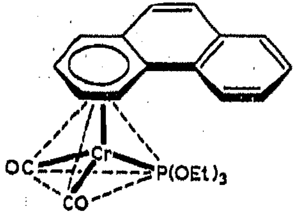
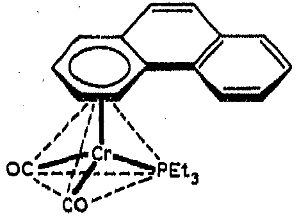
The compounds chosen for X-ray structure determinations were phenanthrenechromium dicarbonyl triethylphosphine and naphthalenechromium dicarbonyl triphenylphosphite. Partial molecular diagrams and selected bond lengths for the two complexes are shown in Fig. 1 and 2 respectively and structure views (ORTEP diagrams, are given in Fig. 3 and 4. Detailed crystallographic data will be published elsewhere [9]. A comparison of the pertinent bond

(continued on p. 108)

TABLE 2

HYDROGENATION OF NORBORNADIENE WITH PHENANTHRENECr(CO)$_2$L CATALYSTS [a]

Catalyst	Init. Conc. moles/lit.	Reaction time (h)	Composition of reaction mixture (%)			
			Norbornadiene	Nortricyclene	Norbornene	Norbornane
	1×10^{-3}	3	0	38	43	19
	1×10^{-3}	2 (130°C)	0	80	20	0
	5×10^{-3}	8	90	5	2	2
		30	70	12	15	3

	4 X 10^{-3}	8 30	98 70	<1 15	<1 8	<1 7
	6 X 10^{-3}	15 (150°C)	100		no reaction	
	5 X 10^{-3}	15	100		no reaction	

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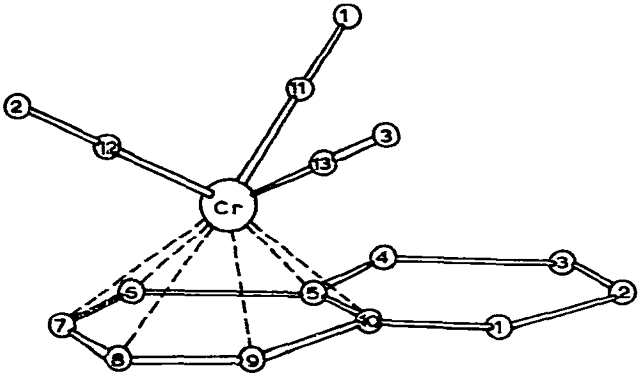
[a] Reaction conditions: 0.1 *M* norbornadiene, 700 psi H_2, 170°C, in cyclohexane.



Bond between atoms	NaphCr(CO)$_3$(Å) [a]	NaphCr(CO)$_2$P(OPh)$_3$(Å)
Cr—C(5)	2.306	2.310
Cr—C(6)	2.186	2.182
Cr—C(7)	2.191	2.185
Cr—C(8)	2.213	2.218
Cr—C(9)	2.214	2.224
Cr—C(10)	2.337	2.329
Cr—C(11)	1.815	1.805
Cr—C(12)	1.830	1.833
Cr—X(13)	1.818	2.217
C(11)—O(1)	1.147	1.173
C(12)—O(2)	1.137	1.160
X(13—O(3)	1.167	

[a] Data taken from Ref. 12.

Fig. 2. Partial molecular diagram and bond distances for naphthaleneCr(CO)$_2$P(OC$_6$H$_5$)$_3$.

lengths in phenanthreneCr(CO)$_3$ with those in phenanthreneCr(CO)$_2$PEt$_3$ (Fig. 1) shows that overall the two complexes have very similar features. The Cr(CO)$_3$ complex was found [10,11] to have one set of four Cr—C (ring) bonds with an average length of 2.209 ± 0.002 Å and one set of two Cr—C (ring) bonds with an average length of 2.289 ± 0.000 Å, the difference between the two sets being a significant 0.080 Å. In the Cr(CO)$_2$PEt$_3$ complex a similar distribution of bond lengths was observed: a set of four Cr—C (ring) bond lengths with an average value of 2.190 ± 0.025 Å and a set of two Cr—C (ring) bond lengths with an average value of 2.305 ± 0.024 Å, showing a difference of 0.11 Å between the two sets (in fact in the latter complex one can distinguish three sets of two bond lengths each: one of 2.170 ± 0.006 Å, one of 2.210 ± 0.016 Å and one of 2.305 ± 0.024 Å). Whilst recognizing the limitations of correlating small changes in metal—C (ring) bond lengths with the donor-acceptor properties of various ligands in areneCr(CO)$_2$L complexes, it is reasonable to conclude that the introduction of the good donor-poor acceptor phosphorus ligand in place of the poor donor-good acceptor CO group has very little effect on the overall bonding interactions in the metal—ring moiety as judged by the metal—C (ring) bond lengths. Consequently, if, as has been suggested [3], the set of longer Cr—C (ring) bonds in phenanthreneCr(CO)$_3$ is the site of attack by the coordinating solvent (or by the diene substrate) in the proposed mechanism for the catalyzed hydrogenation reaction [1,3,5,6] one would expect that, all other factors being equal, the same should hold true for the phenanthrene$Cr(CO)_2PEt_3$ complex. However, it has been found experimentally that the phosphinated complex is very inferior to the tricarbonyl derivative in its catalytic efficiency for the hydrogenation of dienes, as shown by the results described below and summarized in Table 2.

In view of the numerous results already available to us for the hydrogenation using norbornadienes as substrate [3—6], we employed the latter diene for testing the catalytic properties of the new complexes. A non-coordinating solvent, cyclohexane, was used because it was found that solvents such as THF cause rather extensive decomposition of the phosphorylated complexes under the conditions required (170°C and 50 atm pressure) for hydrogenation to proceed. Phenanthrene$Cr(CO)_3$ catalyzes the quantitative hydrogenation of norbornadiene at 130°C in cyclohexane in 2 h to yield the previously observed [6] product distribution (80% notricyclene and 20% norbornene).

Quantitative conversion but a different product distribution (38% nortricyclene, 43% norbornene and 19% norbornane) was observed with the same catalyst at 170°C. We ascribe this change in product distribution, and in particular the appearance of the fully hydrogenated product, norbornane, to partial decomposition of the catalyst under the relatively drastic (high temperature) conditions of the reaction. We have previously reported [2] that formation of chromium oxides from decomposition of arenechromium tricarbonyl complexes impairs the regioselectivity properties of these catalysts and the initial selectively-formed monoolefins undergo further hydrogenation to yield the fully hydrogenated products. When the complex phenanthrene$Cr(CO)_2PEt_3$ was used as catalyst under the same conditions, no hydrogenation occured even after 15 h. With phenanthrene$Cr(CO)_2P(C_6H_5)_3$ about 10% hydrogenation was observed after 8 h and 30% hydrogenation after 30 h, with a product distribution similar to that for the tricarbonyl complex. As shown in Table 2, the phenanthrene$Cr(CO)_2L$ complexes with other phosphorus ligands ($L = P(OC_6H_5)_3$ and $P(OEt)_3$) were just as ineffective in catalyzing the hydrogenation of norbornadiene.

A similar comparison (vide supra) of bond lengths in naphthalene$Cr(CO)_3$ with those in naphthalene$Cr(CO)_2P(OC_6H_5)_3$ (Fig. 2) shows the same resemblance between the two structures as found for the phenanthrene complexes. The naphthalene$Cr(CO)_3$ complex was shown [11,12] to have one set of four Cr—C (ring) bonds with an average length of 2.201 ± 0.014 Å and one set of two Cr—C (ring) bonds with an average length of 2.322 ± 0.022, the difference between the two sets being 0.121. The same two sets of bond lengths in the naphthalene$Cr(CO)_2P(OC_6H_5)_3$ complex were found to be 2.202 ± 0.022 Å and 2.320 ± 0.013 Å and the difference between them 0.118 Å, i.e. nearly identical to that observed with the analogous tricarbonyl complex.

The above results show, therefore, that as in the case of the analogous phenanthrene complex, practically no observable changes occur in the naphthalene—chromium bonding following replacement of a CO group in the tricarbonylchromium complex by a $P(OC_6H_5)_3$ ligand. However, with this phosphorylated complex, just as with the phenanthrene complexes, a profound change in cata-

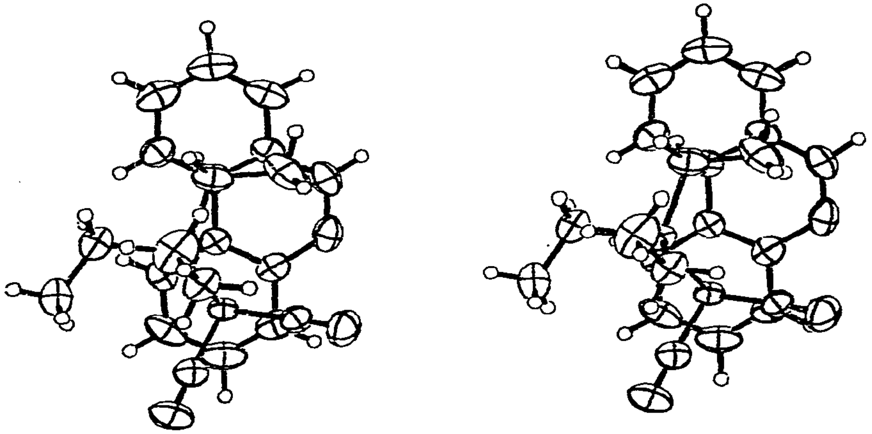


Fig. 3. Stereoscopic view (ORTEP) of phenanthreneCr$(CO)_2P(C_2H_5)_3$.

lytic activity was observed relative to the tricarbonylchromium analogue. Whereas the latter is able to catalyze the hydrogenation of norbornadiene (and other dienes) even at room temperature and normal hydrogen pressure [5,6] and the naphthalene moiety is labilized by coordination solvents such as THF at ambient temperature, the phosphorylated complex does not exhibit any changes in the IR carbonyl stretching region even at 50° C in THF [1,5,6] and induces some hydrogenation of norbornadiene in cyclohexane only at 170° C and 50 atm hydrogen pressure, with a loss of regioselectivity similar to that observed for phenanthreneCr$(CO)_2P(C_6H_5)_3$ (Table 2).

In an attempt to correlate the profound changes in catalytic behaviour of the phosphorylated complexes with the results obtained in the X-ray structural determinations, it appeared to us that the electron density bonding modifications alone could not account for the loss of catalytic activity. A plausible explanation is that the drastic change in catalytic properties for both the phenanthrene and the naphthalene complexes is due largely to steric features, common to both phosphorylated complexes. The triethylphosphine group in the phenanthrene complex (Fig. 3) and, even more strikingly, the triphenylphosphite group in the naphthalene complex (Fig. 4), appear to form a very efficient "umbrella" over the chromium atom, making its coordination sphere practically inaccessible to attack by another ligand, such as a solvent molecule or a diene substrate, as was shown to occur in the hydrogenation reaction catalyzed by the $Cr(CO)_3$ complexes [3—6]. The possibility of a dominant role for the steric characteristics of phosphorus ligands was not unexpected in view of literature reports of such consequences [8]. In a ligand exchange study of Ni^0 complexes using 24 phosphorus ligands L and 12 NiL_4 complexes, Tolman [8] found that there was no correlation between the σ-donor, π-acceptor properties of the various phorphorus ligands and the stability or ease of formation of the NiL_4 complexes. Furthermore, Tolman showed that steric effects were much more important than electronic effects in determining the exchange equilibria among phosphorus ligands on Ni^0 as well as in determining the degree of substitution of CO form $Ni(CO)_4$ by these ligands. In our case, too, the apparently unimportant electronic changes in the Cr—ring bonding, as determined (albeit

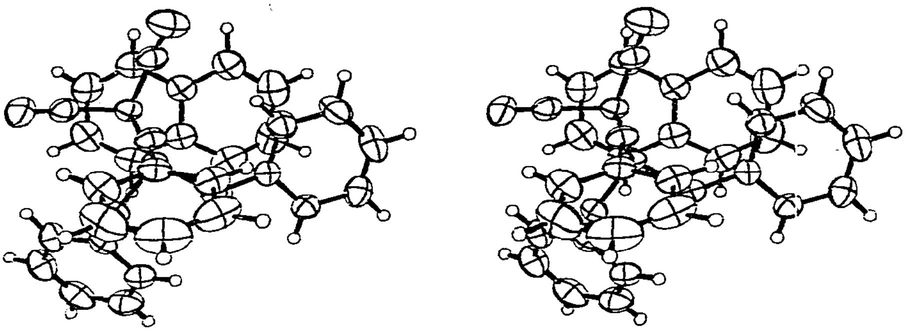


Fig. 4. Stereoscopic view (ORTEP) of naphthaleneCr(CO)$_2$P(OC$_6$H$_5$)$_3$.

grossly) by X-ray bond length measurements, following replacement of a CO by phosphorus ligands in the tricarbonylchromium complexes of phenanthrene and naphthalene cannot explain the drastic catalytic activity changes observed with these compounds. On the other hand, the dominant role of the steric effects introduced by the bulky phosphorus ligands could indicate the correct explanation for the lack of catalytic activity for these complexes. In order to test this hypothesis, the synthesis of phosphorylated chromium complexes of phenanthrene and naphthalene with the stereoelectronically-suitable ligand PF$_3$ [1,8] and the catalytic properties of these complexes are currently being investigated.

Experimental

Apparatus

The spectroscopic and gas chromatography analyses and the hydrogenation experiments were carried out with the instrumentation described in the accompanying publication [1]. The photochemical ligand substitution reactions were performed with a Rayonet photochemical reactor equipped with 16 low pressure (24 W, RPR, 3500 Å) lamps. The mass spectra were measured on Atlas CH-4 and Varian Mat 711 instruments.

Materials

The sources and purification of solvents, hydrogen and diene substrates have been described previously [3,4,6]. The syntheses of areneCr(CO)$_3$ complexes have been published [2—6]. P(C$_6$H$_5$)$_3$, PBu$_3$, P(OC$_6$H$_5$)$_3$,.P(OC$_2$H$_5$)$_3$ and P(OCH$_3$)$_3$ were purchased from Fluka A.G. and PEt$_3$ from Orgmet, Inc. All reactions and column chromatography manipulations (silica gel, Woelm activity I and Florisil 60-100 mesh) were carried out routinely under nitrogen.

Photochemical reactions

All the photochemical ligand substitution reactions were carried out by one or both of the following two general procedures:

General procedure I: A benzene solution of the arenechromium tricarbonyl complex and a 10% molar excess of the substituting ligand was purged for about 20—30 min with dry nitrogen and then subjected to the UV irradiation under continued nitrogen flow. Aliquot samples (1 ml) were removed every 15 min, the solvent evaporated in vacuum, the residue was redissolved in a fixed volume of cyclohexane and the IR spectrum recorded in the region 2100—1700 cm^{-1}. Photolysis was terminated when monitoring of the aliquot samples indicated that the carbonyl absorption of the product had reached a maximum intensity value. The solvent of the total reaction mixture was then evaporated to dryness under reduced pressure and the residue redissolved in a minimum volume of benzene/petroleum ether (1/1) saturated with nitrogen. This solution was then transferred, under nitrogen, to a glass column packed with silica gel or Florisil and eluted under nitrogen with a mixture of benzene/petroleum ether in a 1/1 ratio at first, then gradually increasing the benzene content of the eluting solvent. The elution order of the products was in general: free arene, excess substituting ligand, $-Cr(CO)_5$ and $-Cr(CO)_4$ species arising from disproportionation side-reactions, unreacted arenechromium tricarbonyl and finally the arenechromium dicarbonyl phosphorylated complex. Recrystallization from cyclohexane/petroleum ether afforded the analytical samples (see footnotes to Table 1).

General Procedure II: Freshly distilled THF was delivered, under nitrogen, directly into a Schlenk tube containing the appropriate arene$Cr(CO)_3$ complex. The solution was then subjected to UV irradiation under continued nitrogen flow. The progress of the reaction was followed by monitoring the disappearance of the $\nu(CO)$ A_1 band of the tricarbonyl complex and the appearance of the $\nu(CO)$ A'' band of the arene$Cr(CO)_2$THF complex. When the former absorption peak had almost vanished and the latter appeared to have reached maximum intensity, irradiation was stopped and an equivalent amount of the substituting ligand was added under nitrogen. The reaction solution, usually coloured deep-red, was allowed to stand at room temperature for about 30 min, with continued bubbling of nitrogen through the solution. After evaporating the THF solvent under reduced pressure, the residue was worked-up as in the general procedure I.

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