Ligand Substitution Processes on Carbonylmetal Derivatives. 3.[1] Reaction of Hydridopentacarbonylchromates with Phosphines

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The reaction of $K^+[HCr(CO)_5]^-$ with phosphanes PR_3 (R = Et, Ph, NMe_2) in THF at 65 °C affords the disubstituted complexes *trans*-$Cr(CO)_4(PR_3)_2$ isolated in 57−70% yield. The X-ray crystal structures of *trans*-$Cr(CO)_4(PR_3)_2$ derivatives have been determined for R = Et and NMe_2. These reactions proceed first by exchange of one carbon monoxide ligand, generating the monosubstituted hydridotetracarbonylchromates $K^+[HCr(CO)_4PR_3]^-$, observed and characterized by NMR spectroscopy for R = Et and Ph. The second step involves substitution of the hydride ligand of $K^+[HCr(CO)_4PR_3]^-$ to give the disubstituted derivatives *trans*-$Cr(CO)_4(PR_3)_2$. These ligand exchange processes are discussed and compared with the reaction of phosphanes with the dinuclear bridged $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$.

Introduction

Ligand substitution processes in transition-metal complexes have attracted much attention, both for the design of specific syntheses of heteroleptic complexes and for a contribution to the understanding of reaction mechanisms, particularly the loss of small molecules or ions from low-valent metal complexes.[2,3] In this respect, neutral metal carbonyls, especially iron carbonyls, have been particularly studied.[4]

In the series of iron carbonyls, we were the first to report, some years ago, that the anionic hydrido complex, $K^+[HFe(CO)_4]^-$, **1**, is a very versatile material for the high yield synthesis of a large variety of phosphane-substituted iron carbonyl complexes, most of which were described for the first time.[5] Indeed, depending on the characteristics of the phosphorus ligand (cone angle θ, pK_a) and the nature of the solvent (protic or aprotic), the reaction of **1** with phophites and phosphines (thereafter designated P) highly selectively leads to monosubstituted hydrido complexes $K^+[HFe(CO)_3P]^-$ [6] or neutral disubstituted dihydrido complexes $H_2Fe(CO)_2P_2$,[7−9] but also to disubstituted $Fe(CO)_3P_2$,[10,11] and even trisubstituted $Fe(CO)_2P_3$ complexes.[12] Furthermore, the reaction of **1** with phosphines in THF produced a 1/1 mixture of $Fe(CO)_3P_2$ and $K_2Fe(CO)_4$, which can be easily separated.[6] This reaction constitutes the more convenient preparation of $K_2Fe(CO)_4$,[13] a non-pyrophoric substitute of the Collman reagent, $Na_2Fe(CO)_4$.[14] The reaction mechanisms have been rationalized.[1,6,15] In all cases, the first step is the substitution of a carbon monoxide ligand of $K^+[HFe(CO)_4]^-$, leading to $K^+[HFe(CO)_3P]^-$ complexes. In only one case (P = $P(OMe)_3$, THF as solvent) a second CO substitution was observed, leading quantitatively to the disubstituted hydridoferrate $K^+[HFe(CO)_2P_2]^-$.[1] In other cases, depending on the nature of P and the nature of the solvent, the $K^+[HFe(CO)_3P]^-$ complexes either can be isolated or evolve in situ to selectively afford one of the above neutral complexes.[5]

As part of our interest in the applications of hydridocarbonylmetalates in organic synthesis and homogeneous catalysis,[16,17] we recently investigated the study of the reactivity of the group VI analogue $K^+[HCr(CO)_5]^-$, **2**, in organic synthesis.[18−20] In addition, in light of the

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[1] Part of the Ph.D. Thesis of E. Roblou. For Part 2 of the series, see: Brunet, J.-J.; Commenges, G.; Kindela, F.-B.; Neibecker, D. *Organometallics* **1992**, *11*, 3023−3030.

[2] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1968; Basolo, F. *Inorg. Chim. Acta* **1981**, *50*, 65−70.

[3] Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984,** *53*, 227−259. Luth, T. Y. *Coord. Chem. Rev.* **1984**, *60*, 255−276.

[4] Darensbourg, D. J. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1982; Vol. 21, pp 113−150.

[5] For a review, see: Brunet, J.-J.; Chauvin, R.; Diallo, O.; Kindela, P.; Leglaye, P.; Neibecker, D. *Coord. Chem. Rev.* **1998**, *178−180*, 331−351.

[6] Brunet, J.-J.; Commenges, G.; Kindela, F.-B.; Neibecker, D. *Organometallics* **1992**, *11*, 1343−1350.

[7] Brunet, J.-J.; Kindela, F.-B.; Labroue, D.; Neibecker, D. *Inorg. Chem.* **1990**, *29*, 4152−4153.

[8] Brunet, J.-J.; Kindela, F.-B.; Neibecker, D. *Inorg. Synth.* **1992**, *29*, 156−160.

[9] Arion, V.; Brunet, J.-J.; Neibecker, D. *Inorg. Chem.* **2001**, 2628−2630.

[10] Brunet, J.-J.; Kindela, F.-B.; Neibecker, *J. Organomet. Chem.* **1989**, *368*, 209−212.

[11] Brunet, J.-J.; Kindela, F.-B.; Neibecker, D. *Inorg. Synth.* **1992**, *29*, 151−156.

[12] Brunet, J.-J.; Kindela, F.-B.; Neibecker, D. *Inorg. Synth.* **1996**, *31*, 202−210.

[13] Baby, A.; Brunet, J.-J.; Kindela, F.-B.; Neibecker, D. *Synth. Comm.* **1994**, *24*, 2827−2834.

[14] Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342−347.

[15] Brunet, J.-J.; Kindela, F.-B.; Neibecker, D. *Phosphorus, Sulfur Silicon* **1993**, *77*, 65−68.

[16] Brunet, J.-J. *Chem. Rev.* **1990**, *90*, 1041−1059.

[17] Brunet, J.-J. *Eur. J. Inorg. Chem.* **2000**, 1377−1390.

10.1021/om020130b CCC: $22.00

Table 1. Main NMR Characteristics of the Chromium Carbonyl Derivatives[a,b]

compound	$^{31}P\{^1H\}$ δ (ppm)	^1H δ (ppm), *J* (Hz)	compound	$^{31}P\{^1H\}$ δ (ppm)
$KHCr(CO)_5$		−6.97	$Cr(CO)_5PEt_3$	37.9
$KHCr(CO)_4PEt_3$	54.6	−7.07 (d), 38	$Cr(CO_4(PEt_3)_2$	51.8
$KHCr(CO)_4PPh_3$	80.9	−6.25 (d), 35	$Cr(CO)_5PPh_3$	59.0
$KHCr_2(CO)_{10}$		−19.49	$Cr(CO)_4(PPh_3)_2$	78.0
$KHCr_2(CO)_9PEt_3$		−17.85(d), 26	$Cr(CO)_5P(NMe_2)_3$	159.5
$KHCr_2(CO)_8(PEt_3)_2$[c]		−17.16 (t), 39	$Cr(CO)_4[P(NMe_2)_3]_2$	177.8
$KHCr_2(CO)_9PPh_3$		−7.23 (d), 24	$Cr(CO)_5[HP(NMe_2)_2]$[d]	137.8

[a] In THF-d_8 unless otherwise noted. [b] As references, the $^{31}P\{^1H\}$ chemical shift of the free ligands were the following: PEt_3, $\delta = -18.5$ ppm; PPh_3, $\delta = -1.5$ ppm; $P(NMe_2)_3$, $\delta = 121.9$ ppm. [c] In CD_3CN. [d] ^1H NMR: $\delta = 6.84$ ppm (d), $^1J_{H-P} = 398$ Hz.

coordination chemistry developed with **1**, we were obviously interested in examining the reaction of **2** with phosphanes. In a short comparative study of the coordination chemistry of **1** and **2**, we already noticed some differences, which were tentatively attributed to the lower acidity of **2** as compared to that of **1**.[18] We report here full details of the reaction of **2** with PEt_3, PPh_3, and $P(NMe_2)_3$. The goal of this study was to examine the possible synthetic interest of these reactions, but also to gain more insight into the ligand substitution processes on hydridocarbonylmetalates.

Results and Discussion

Contrary to $K^+[HFe(CO)_4]^-$, which is stable in protic media, $K^+[HCr(CO)_5]^-$ reacts with alcohols to generate the stable bridged dinuclear hydride $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$, **3**, with loss of molecular hydrogen.[5,21] Thus, only reactions of **2** in aprotic solvents have been considered. Reactions of $(\mu\text{-}H)[Cr(CO)_5]_2^-$ (Et_4N^+ salt) with phosphines have been reported before[22,23] and will be discussed comparatively.

Reaction of 2 with Triethylphosphine ($\theta = 132°$). The reaction of **2** with 1 equiv of PEt_3 in THF at 55 °C was monitored by $^{31}P\{^1H\}$ NMR. After 2 h reaction, besides the signal of unreacted PEt_3 ($\delta = -18.5$ ppm), two new signals were observed at 54.6 ppm (major) and 51.8 ppm (minor). After 4 h, the signal at 51.8 ppm had increased, and after 23 h, all the phosphine had been consumed to leave only the signal at 51.8 ppm, together with very small signals at 40.9 and 35.5 ppm. None of the above signals corresponded to the monosubstituted complex $Cr(CO)_5PEt_3$ ($\delta = 37.9$ ppm), prepared independently according to a literature procedure.[24] The signal at 51.8 ppm could be attributed to the disubstituted complex *trans*-$Cr(CO)_4(PEt_3)_2$, **4** (vide infra). It must be noted that, in this reaction, the fate of half of the chromium species has not been determined. However, when the reaction was performed with 2 equiv of PEt_3 in THF at 65 °C, a similar progress was observed and **4** was the only product formed (quantitative consumption of PEt_3). This reaction can thus be formally represented by eq 1. The reaction product **4** (yellow solid) could be isolated analytically pure in 70% yield and fully characterized (Table 1). Moreover, suitable single crystals were obtained, and the structure of **4** was established by X-ray diffraction (Figure 1, Table 2).

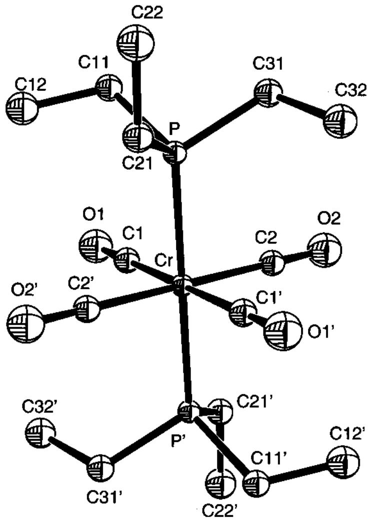

Figure 1. Molecular structure of complex **4** with atom-labeling scheme. Ellipsoids represent 50% probability. Selected bond lengths (Å) and angles (deg): Cr−P 2.329(1); Cr−C(1) 1.863(3); Cr−C(2) 1.869(3); P−C(11) 1.839(3); P−C(21) 1.845(3); P−C(31) 1.836(3); C(1)−Cr−C(2) 91.1(1); C(1)−Cr−C(2)′ 88.9(1) [Symmetry transformations used to generate equivalent atoms: −*x*+1, −*y*, −*z*].

$$\underset{\mathbf{2}}{K^+[HCr(CO)_5]^-} + 2\,PEt_3 \xrightarrow[72\ h]{THF,\ 65°C} \underset{\mathbf{4}}{trans\text{-}Cr(CO)_4(PEt_3)_2} + KH + 2\,CO \qquad (1)$$

This result is in contrast with the chemistry developed with the hydridocarbonylferrate **1**. Indeed, the reaction of **1** with phosphines (PPh_3, PBu_3) in THF occurs as shown by eq 2, and the yield of the disubstituted complex $Fe(CO)_3(PR_3)_2$ cannot exceed 50%.[6]

$$2\,K^+[HFe(CO)_4]^- + 2\,PR_3 \xrightarrow{THF,\ 65°C} Fe(CO)_3(PR_3)_2 + K_2Fe(CO)_4 + CO + H_2 \qquad (2)$$

In reaction 2, the monosubstituted hydride $[HFe(CO)_3PR_3]^-$ complex formed in the first step is sufficiently basic to deprotonate $[HFe(CO)_4]^-$, yielding the dianionic species $[Fe(CO)_4]^{2-}$ and a neutral dihydride $H_2Fe(CO)_3PR_3$. The latter is not stable at the reaction temperature and loses H_2 to generate the unsaturated

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[18] Brunet, J.-J.; Chauvin, R.; Leglaye, P. *J. Organomet. Chem.* **1998**, *571*, 7−13.

[19] Brunet, J.-J.; Chauvin, R.; Leglaye, P. *Eur. J. Inorg. Chem.* **1999**, 713−716.

[20] Andrieu, B.; Brunet, J.-J.; Diallo, O.; Donnadieu, B.; Lienafa, J.; Roblou, E. *J. Organomet. Chem.* **2002**, *643−44*, 27−31.

[21] Marko, L.; Nagy-Magos, N. *J. Organomet. Chem.* **1985**, *285*, 193−203.

[22] Darensbourg, M. Y.; Walker, N. *J. Organomet. Chem.* **1976**, *117*, C68−C74.

[23] Darensbourg, M. Y.; Walker, N.; Burch, R. R. *Inorg. Chem.* **1978**, *17*, 52−56.

[24] Vincent, E.; Verdonk, L.; Van der Kelen, G. P. *J. Mol. Struct.* **1980**, *69*, 33−40.

Table 2. Crystal Data and Structure Refinement for Complexes 4 and 12

identification code	**4**	**12**
empirical formula	$C_8H_{15}Cr_{0.5}O_2P$	$C_{16}H_{36}CrN_6O_4P_2$
fw	200.17	490.45
temperature	180(2) K	180(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a, Å	7.540(5)	15.4663(13)
b, Å	7.719(5)	13.7007(11)
c, Å	9.138(5)	23.544(2)
α, deg	108.086(5)	90°
β, deg	96.328(5)	90°
γ, deg	91.565(5)	90°
volume	501.4(5) Å^3	4989.0(7) Å^3
Z	2	8
density (calcd)	1.326 Mg/m^3	1.306 Mg/m^3
abs coeff	0.744 mm^{-1}	0.618 mm^{-1}
F(000)	212	2080
cryst size	0.5 × 0.37 × 0.13 mm^3	0.37 × 0.25 × 0.13 mm^3
θ range for data collection	3.82° to 24.38°	3.27° to 20.81°
index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-10 \le l \le 10$	$-15 \le h \le 13$, $-13 \le k \le 13$, $-22 \le l \le 23$
no. of reflns collected	4037	18 034
no. of ind reflns	1520 [*R*(int) = 0.0217]	2600 [*R*(int) = 0.1760]
completeness to $\theta = 24.38°$	92.3%	99.4%
abs corr	empirical (DIFABS)	empirical (DIFABS)
max. and min. transmn	0.8720 and 0.5770	0.6826 and 0.2171
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	1520/0/49	2600/0/274
goodness-of-fit on F^2	1.071	1.150
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0455, wR2 = 0.1098	R1 = 0.0733, wR2 = 0.1216
R indices (all data)	R1 = 0.0482, wR2 = 0.1118	R1 = 0.1118, wR2 = 0.1376
largest diff peak and hole	0.658 and −0.520 e Å^{-3}	0.250 and −0.280 e Å^{-3}

species "$Fe(CO)_3(PR_3)$", which is finally scavenged by the phosphine to afford $Fe(CO)_3(PR_3)_2$ in ≤50% yield.

Formation of **4** in 70% isolated yield (eq 1) thus suggests that, if it is generated, the monosubstituted complex $K^+[HCr(CO)_4PEt_3]^-$ does not react as its analogue in the iron series. To try to gain more insight on this point, the reaction of **2** with PEt_3 (2 equiv) was conducted in THF-d_8 in a sealed NMR tube and monitored by both ^{31}P and ^1H NMR. After 10 h at room temperature, the $^{31}P\{^1H\}$ NMR spectrum indicated the appearance of the signals at 54.6 and 51.6 ppm, while the major signal was that of unreacted PEt_3. Interestingly, the ^1H NMR spectrum (hydrides region) exhibited two signals, a major one at − 6.97 ppm ($KHCr(CO)_5$) and a minor one (ca. 10%) at − 7.12 ppm. In fact, the latter corresponded to a doublet, one branch of which is buried beneath the signal at − 6.97 ppm. Indeed, selective irradiation experiments evidenced the coupling of this hydride ($\delta = -7.05$ ppm, d, $^2J_{H-P} = 38$ Hz) with the phosphorus atom, giving the 54.6 ppm signal (d) in the ^{31}P NMR spectrum. These signals are attributed to the monosubstituted hydridotetracarbonylchromate $K^+[HCr(CO)_4PEt_3]^-$, **5** (eq 3). Indeed, the ^1H NMR chemical shift of the substituted hydride **5** is close to that of **2**, as already observed in the tungsten series ($[HW(CO)_5]^-$, $\delta = -4.2$ ppm; $[HW(CO)_4PMe_3]^-$, $\delta = -3.6$ ppm).[25] Moreover, this assignment is also supported by the fact that the possible mono- and disubstituted dinuclear complexes $K^+(\mu\text{-}H)[Cr(CO)_5][Cr(CO)_4PEt_3]^-$ and $K^+(\mu\text{-}H)[Cr(CO)_4PEt_3]_2^-$ have been observed in independent experiments (vide infra) and exhibit ^1H NMR chemical shifts close to that of the parent unsubstituted dinuclear hydride **3**, as previously observed in the molybdenum series.[23] Heating the NMR tube at 65 °C allowed observation of the slow consumption of **2**, **5**, and PEt_3 to give **4** (part of which precipitated as yellow crystals) (eq 4), contaminated by some traces of an unidentified compound exhibiting a ^{31}P NMR signal at 35.5 ppm. The overall results can be summarized by eqs 3 and 4.

$$\underset{\mathbf{2}}{K^+[HCr(CO)_5]^-} + PEt_3 \longrightarrow \underset{\mathbf{5}}{K^+[HCr(CO)_4(PEt_3)]^-} + CO \quad (3)$$

$$\underset{\mathbf{5}}{K^+[HCr(CO)_4PEt_3]^-} + PEt_3 \longrightarrow \underset{\mathbf{4}}{\textit{trans}\text{-}Cr(CO)_4(PEt_3)_2} + KH \quad (4)$$

During these experiments, we could observe that **2** was stable for at least 2 days in THF-d_8 at 65 °C (in the presence of liberated carbon monoxide) without observable transformation to $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$. Furthermore, the reaction seemed slow to the end, an observation that could be related to the fact that, in a sealed tube, the displaced carbon monoxide cannot be exhausted and may decrease the rate of the substitution processes. Last, we believed that **5** did not react with **2** at a significant rate since they could be observed together (^1H NMR analysis) for long reaction times. This observation became still more obvious when the reaction was conducted in CD_3CN. In this case, we could observe by ^1H NMR a mixture of **2** and **5** for several hours at 65 °C, whereas the consumption of PEt_3 was slow.

Formation of disubstituted $M(CO)_4(PPh_3)_2$ complexes (M = Cr, Mo, W) is known to occur when the corre-

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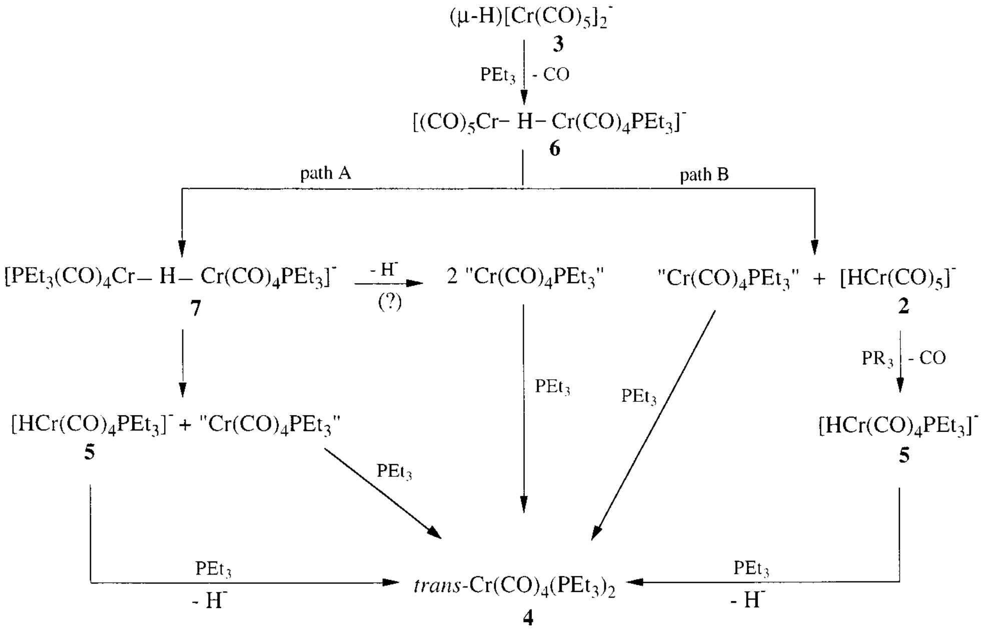
(25) Slater, S. G.; Lusk, R.; Schuman, B. F.; Darensbourg, M. Y. *Organometallics* **1982**, *1*, 1662−1666.

Scheme 1



sponding hexacarbonyl $M(CO)_6$ is reacted with the phosphine (5 equiv) in the presence of $NaBH_4$ (4 equiv) in ethanol.[26] Although the exact mechanism involved in these reactions is not known, Darensbourg et al. have reported convincing data indicating that the dinuclear hydride $Na^+(\mu\text{-H})[Cr(CO)_5]_2^-$ may be the intermediate on which the carbonyl substitution occurs, either in ethanol or in THF.[23] Since $K^+(\mu\text{-H})[Cr(CO)_5]_2^-$, **3**, may result from the evolution of **2**,[17] we were interested in comparing the reaction of PEt_3 with **2** and **3** under the same conditions. Thus, the reaction of **3** (free of any trace of **2**) with 4 equiv of PEt_3 was performed in CD_3CN in a NMR sealed tube at room temperature. The ^1H NMR monitoring of the reaction showed interesting features. After 10 h, we could observe unreacted **3** (s, $\delta = -19.49$ ppm), but also significant amounts of **2** (s, $\delta = -6.97$ ppm). Later on (78 h), we could observe simultaneously **3** and **2**, but also the monosubstituted mononuclear derivative $K^+[HCr(CO)_4PEt_3]^-$, **5** (vide supra), the monosubstituted dinuclear complex $K^+(\mu\text{-H})[Cr(CO)_4PEt_3][Cr(CO)_5]^-$, **6** (d, $\delta = -17.85$ ppm, $^2J_{H-P} = 26$ Hz), and the disubstituted dinuclear complex $K^+(\mu\text{-H})[Cr(CO)_4PEt_3]_2^-$, **7** (t, $\delta = -17.16$ ppm, $^2J_{H-P} = 39$ Hz). Unexpectedly, the ^{31}P NMR spectra indicated the formation of both the mono- and the disubstituted neutral complexes $Cr(CO)_5PEt_3$ and *trans*-$Cr(CO)_4(PEt_3)_2$ in nearly equivalent amounts. This observation may be related to the fact that the reaction was performed in a sealed tube, so that the displaced carbon monoxide was still present, and thus might compete with the phosphine in the reaction with the unsaturated "$Cr(CO)_4PEt_3$" intermediate (Scheme 1). A similar observation has been mentioned by Darensbourg et al.[22] We have verified independently that the monosubstituted complex $Cr(CO)_5PEt_3$ did not afford significant amounts of **4** when reacted with 2 equiv of PEt_3 for 3 days in THF at 65 °C.

These observations strongly support the mechanism proposed by Darensbourg et al.[23] (Scheme 1) and prove that, besides path A, the suggested path B, through $[HCr(CO)_5]^-$ (resulting from the disruption of the dinuclear monosubstituted hydride), effectively occurs. It must be noted that, as suggested by one reviewer, the likelihood that hydride would be extracted from the binuclear complex **7** is small. In contrast, the disruption of **7** into **5** and the 16-electron "$Cr(CO)_4PEt_3$" species seems more reasonable than generating two 16-electron "$Cr(CO)_4PEt_3$" species simultaneously.

The reaction of PEt_3 with $[HCr(CO)_5]^-$ thus occurs by *direct* substitution of a carbonyl ligand by the phosphine, generating the observable intermediate **5**, followed by substitution of the hydride ligand by another molecule of the phosphine. Since $[HCr(CO)_5]^-$ is hexacoordinate, the first step probably involves dissociation of the CO ligand favored as the temperature increases. For neutral carbonylmetals, another well-known way to promote carbon monoxide dissociation is photochemical activation.[27] To the best of our knowledge, such an activation has never been reported for anionic carbonylmetal species. When the reaction of **2** with 2 equiv of PEt_3 was conducted at room temperature under irradiation (365 nm), a slow reaction occurred during which we could observe the intermediate **5** (NMR monitoring). The latter is slowly consumed to give the expected complex **4**, together with the trisubstituted derivative *mer*-$Cr(CO)_3(PEt_3)_3$, **8**, identified on the basis of its $^{31}P\{^1H\}$ NMR characteristics ($\delta_{trans} = 48.2$ ppm, d, $^2J_{P-P} = 22$ Hz and $\delta_{cis} = 35.1$ ppm, t, $^2J_{P-P} = 22$ Hz).

Reaction of 2 with Triphenylphosphine PPh_3 ($\theta = 145°$). The reaction of **2** with 2 equiv of triphenylphosphine in THF proceeds as that with triethylphosphine. The reaction is extremely slow at room temperature, but proceeds in refluxing THF. Monitoring the reaction by ^{31}P NMR allowed the observation of the formation of the expected intermediate $K^+[HCr(CO)_4PPh_3]^-$, **10** (THF-d_8, $\delta = 80.9$ ppm, $^2J_{P-H} = 35$ Hz), already fully characterized as the *cis* H−Cr−P isomer.[18] Classical workup after 72 h reaction in refluxing THF

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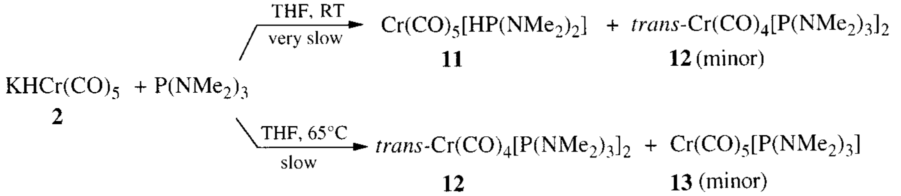
(26) Chatt, J.; Leigh, G. J.; Thankarajan, N. *J. Organomet. Chem.* **1971**, *297*, 105−110.

(27) For a recent paper, see: Bergstrom, C. L.; Luck, R. L. *Inorg. Chim. Acta* **2001**, *318*, 77−83, and references therein.

Scheme 2



allowed the recovery of unreacted triphenylphosphine (60%) and the disubstituted complex *trans*-$Cr(CO)_4(PPh_3)_2$, **9** (analytically pure, 25% yield) (eq 5), which could be fully characterized (Table 1). The X-ray structure of **9** has been reported recently.[28]

$$\underset{\textbf{2}}{K^+[HCr(CO)_5]^-} + 2\ PPh_3 \xrightarrow[72\ h]{THF,\ reflux} \underset{\textbf{9}}{trans\text{-}Cr(CO)_4(PPh_3)_2} + KH + 2\ CO \quad (5)$$

Reaction of 2 with Tris(dimethylamino)phosphine ($\theta = 157°$). The reaction of $K^+[HFe(CO)_4]^-$ with $P(NMe_2)_3$ does not proceed like that with PR_3 or PAr_3. Indeed, instead of promoting the substitution of a carbonyl ligand of **1** by $P(NMe_2)_3$, the reaction occurs by attack of **1** on the phosphorus atom (substitution of a "NMe_2" group) to give the monosubstituted *secondary* phosphine complex $Fe(CO)_4[HP(NMe_2)_2]$ with simultaneous formation of an equivalent molecular amount of $K_2Fe(CO)_4$ (eq 6).[29]

$$2\ KHFe(CO)_4 + P(NMe_2)_3 \xrightarrow{THF,\ RT} K_2Fe(CO)_4 + Fe(CO)_4[HP(NMe_2)_2] + Me_2NH \quad (6)$$

We have briefly reported that the reaction of **2** with $P(NMe_2)_3$ is very slow at room temperature, but that if $P(NMe_2)_3$ is first treated (independently) by AcOH, the reaction rapidly affords the corresponding monosubstituted complex $Cr(CO)_5[HP(NMe_2)_2]$, **11** (eq 7).[18] These observations have been explained by the lower acidity of **2** as compared to that of **1** (toward $P(NMe_2)_3$).

$$KHCr(CO)_5 + P(NMe_2)_3/AcOH \xrightarrow{THF,\ RT} \underset{\textbf{11}}{Cr(CO)_5[HP(NMe_2)_2]} + AcOK + Me_2NH \quad (7)$$

Studying the reaction of $P(NMe_2)_3$ with **2** in more detail indicated that the reaction at room temperature in THF very slowly generates **11** (^{31}P NMR, $\delta = 137.8$ ppm, d, $^1J_{P-H} = 398$ Hz, ^1H NMR, $\delta = 6.84$ ppm, d, $^1J_{H-P} = 398$ Hz) together with smaller amounts of *trans*-$Cr(CO)_4[P(NMe_2)_3]_2$, **12** ($^{31}P\{^1H\}$ NMR, $\delta = 177.8$ ppm) (Scheme 2). In contrast, if the reaction was performed in THF at 65 °C, **11** was not formed (Scheme 2). The reaction slowly afforded a mixture of **12** and, unexpectedly, the known monosubstituted derivative $Cr(CO)_5P(NMe_2)_3$, **13** ($^{31}P\{^1H\}$ NMR, $\delta = 159.5$ ppm), in a ca. 90/10 ratio.[30] However, even long reaction times (100 h) did not promote complete consumption of $P(NMe_2)_3$.

These results suggest that at room temperature the major reaction is the nucleophilic attack of the hydride ligand of **2** (already hexacoordinated) at the phosphorus atom of the phosphine, a reaction that is greatly accelerated if performed on a protonated form of $P(NMe_2)_3$ (eq 7). In contrast, at higher temperatures, dissociation of a carbonyl ligand of **2** may be favored, and the direct ligand exchange at the chromium site proceeds to form **12**. Note that, contrary to what was observed with PEt_3 and PPh_3, we could not detect the expected intermediate $K^+[HCr(CO)_4P(NMe_2)_3]^-$, which might be rapidly converted to the neutral disubstituted derivative *trans*-$Cr(CO)_4[P(NMe_2)_3]_2$. Interestingly, when **2** was reacted with $P(NMe_2)_3$ (2 equiv) under irradiation (365 nm), a quantitative reaction was observed, within 38 h, affording **12** selectively (57% isolated yield) (eq 8). Single crystals of **12** were obtained, and the structure was determined by X-ray analysis (Figure 2, Table 2).

$$\underset{\textbf{2}}{KHCr(CO)_5} + 2\ P(NMe_2)_3 \xrightarrow[38\ h]{THF,\ h\nu} \underset{\textbf{12}}{trans\text{-}Cr(CO)_4[P(NMe_2)_3]_2} \quad (8)$$

General Comments

Recently reported theoretical studies[31] on the effect of ligands X on the CO labilization in $[XM(CO)_5]^-$ complexes (M = Cr, Mo, W) indicate that CO dissociation energies increase in the series $X = NH_2 < OH, Cl < Me < H$ (i.e., π-donor ligands favor CO dissociation much more than σ-donor ones) and that CO loss is easier from the *cis* position. Although these studies do not take into account the well-known selective site ion-pairing interactions,[32,33] the calculations are in agreement with experimental data. As a matter of fact, CO substitution on $[ClCr(CO)_5]^-$ by phosphines and phosphites easily occurs at room temperature (eq 9).[34]

$$[Et_4N]^+[ClCr(CO)_5]^- + PBu_3 \xrightarrow[RT,\ 10\ mn]{THF} [Et_4N]^+[ClCr(CO)_4(PBu_3)]^- + CO \quad (9)$$

The results obtained in the present study show that, in agreement with the theoretical study, the CO sub-

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[28] Bao, J.; Geib, S. J.; Cooper, N. J. *J. Organomet. Chem.* **2001**, *631*, 188192.

[29] Brunet, J. J.; Chauvin, R.; Neibecker, D. *Synth. Commun.* **1997**, *27*, 1433−1437.

[30] Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur* **1979**, *6*, 377−389.

[31] Macgregor, S. A.; MacQueen, D. *Inorg. Chem.* **1999**, *38*, 4868−4876.

[32] Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 222−274.

[33] Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871−876.

[34] Wolkulich, M. J.; Atwood, J. D. *Inorg. Synth.* **1985**, *23*, 37−41.

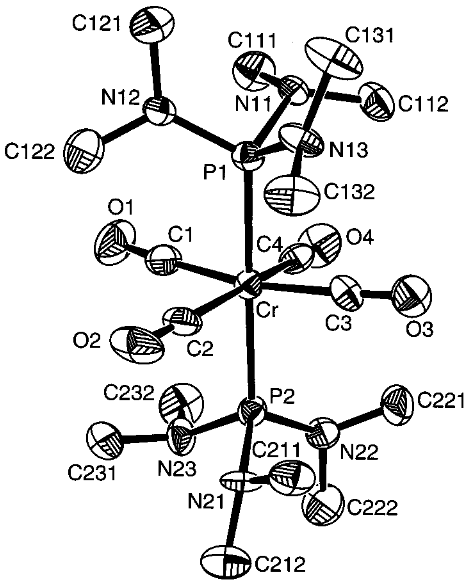

Figure 2. Molecular structure of complex **12** with atom-labeling scheme. Ellipsoids represent 50% probability. Selected bond lengths (Å) and angles (deg): Cr(1)−C(1) 1.854(9); Cr(1)−C(3) 1.858(8); Cr(1)−C(4) 1.863(8); Cr(1)−C(2) 1.888(8); Cr(1)−P(1) 2.349(2); Cr(1)−P(2) 2.356(2); P(1)−N(13) 1.674(6); P(1)−N(12) 1.677(6); P(1)−N(11) 1.698(6); P(2)−N(22) 1.682(6); P(2)−N(23) 1.689(6); P(2)−N(21) 1.691(6); C(1)−Cr(1)−C(3) 168.9(3); C(1)−Cr(1)−C(4) 82.0(3); C(3)−Cr(1)−C(4) 89.7(3); C(1)−Cr(1)−C(2) 89.7(3); C(3)−Cr(1)−C(2) 99.4(3); C(4)−Cr(1)−C(2) 169.3(3); C(1)−Cr(1)−P(1) 89.0(2); C(3)−Cr(1)−P(1) 84.5(2); C(4)−Cr(1)−P(1) 95.1(2); C(2)−Cr(1)−P(1) 91.3(2); C(1)−Cr(1)−P(2) 94.4(2); C(3)−Cr(1)−P(2) 92.6(2); C(4)−Cr(1)−P(2) 88.3(2); C(2)−Cr(1)−P(2) 85.7(2); P(1)−Cr(1)−P(2) 175.53(8).

stitution on $[HCr(CO)_5]^-$ is more difficult than that on $[ClCr(CO)_5]^-$ (vide supra), but does occur selectively (i.e., without substitution of the hydride ligand, which would have generated the $Cr(CO)_5PR_3$ derivatives). Under the conditions used, the monosubstituted hydridochromate $[HCr(CO)_4PR_3]^-$ further evolves by substitution of the hydride ligand by the phosphine, a reaction that is related to that reported for $[ClCr(CO)_4PR_3]^-$ (eq 10)[34] or for $[AcOMo(CO)_4PPh_3]^-$.[35]

$$[Et_4N]^+[ClCr(CO)_4PBu_3]^- + PPh_3 \xrightarrow[\text{RT, 1 h}]{CH_2Cl_2} trans\text{-}[Cr(CO)_4PBu_3(PPh_3)] + Et_4NCl \quad (10)$$

It has long been established that for the reaction of hydridometalates $[HM(CO)_5]^-$ (M = Cr, Mo, W) with primary alkyl halides, the tendency of hydride (H^-) transfer vs SET processes is increased by substitution of a carbonyl ligand by a less effective π-acceptor one like phosphines or phosphites.[36] This effect has been explained by the decreased ability of the hydride ligand to give electrons to the metal in the presence of a good σ-donor ligand such as a phosphane. This reactivity order also parallels the increased tendency for alkali metal cations to interact with the hydride metal site rather than with a carbonyl oxygen site. Such an interaction with the hydride site results in a decrease of the H−M⁻ bond, thus favoring H^- exchanges. The observed reactivities of **2** and of the intermediates $K^+[HCr(CO)_4PR_3]^-$ toward phosphines are in agreement with the above considerations.

Experimental Section

Methods and Materials. All sample manipulations were carried out under argon using standard Schlenk tube and vacuum techniques. Solvents and solutions were transferred via syringe or cannula. Tetrahydrofuran (SDS) was distilled over Na/benzophenone. Acetonitrile was distilled over P_2O_5 under argon and stored over 3 Å molecular sieves. $KHCr(CO)_5$[18] and $KHCr_2(CO)_{10}$[37] were prepared according to reported procedures. Chromium hexacarbonyl (Strem Chemicals) and phosphines (Strem Chemicals or Fluka) were used without further purification. Argon U (L'Air Liquide) was used after passage through molecuar sieves.

Instumentation. Irradiations were performed with an external 2 × 15 W lamp (312−365 nm). Infrared spectra were recorded on a Perkin-Elmer 1725 IRFT spectrometer using CaF_2 windows (0.05 mm). ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Brücker AC 200, AM 250, DPX 300, or AMX 400 apparatus.

Reactions. Thermal Activation. The reaction procedures is exemplified in the case of triethylphosphine: In a Schlenk tube, triethylphosphine (3.41 mmol) was added to $KHCr(C0)_5$ (solid, 1.66 mmol), and freshly distilled THF (30 mL) was added. The solution was magnetically stirred for 3 days at 67 °C (oil bath). The solvent was then evaporated under reduced pressure and the reaction product, $Cr(CO)_4(PEt_3)_2$, extracted with 5 × 40 mL of hexane (yield 70%). X-ray suitable crystals were obtained by slow crystallization from a THF/hexane (1/4) solvent mixture.

Photochemical Activation. The reaction procedure is exemplified in the case of tris(dimethylamino)phosphine: In a quartz Schlenk tube, tris(dimethylamino)phosphine (2.57 mmol) was added to $KHCr(C0)_5$ (solid, 1.28 mmol), and freshly distilled THF (24 mL) was added. The solution was irradiated (365 nm) for 38 h. The solvent was then evaporated under reduced pressure and the reaction product extracted with large amounts (13 × 40 mL) of hexane (yield 57%). X-ray suitable crystals were obtained by slow crystallization from a THF/hexane (1/10) solvent mixture.

X-ray Crystallographic Study. Data for compound **4** were collected on a Stoe IPDS diffractometer, whereas an Oxford-Diffraction Xcalibur diffractometer was used for **12**. The final unit cell parameters were obtained by the least-squares refinement of 8000 and 18 034 reflections for **4** and **12**, respectively. For both compounds, only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR97)[38] and refined by least-squares procedures on F^2. In both compounds, all H atoms were introduced at calculated positions as riding atoms [$d(CH) = 0.99-0.98$ Å], using AFIX23 for CH_2 and AFIX137 for CH_3 groups, with a displacement parameter equal to 1.2 (CH_2) or 1.5 (CH_3) times that of the parent atom. Least-squares refinements were carried out by minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R = \sum(||F_o| - |F_c||)/\sum(|F_o|)$ and $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$, having values listed in Table 2.

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(35) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398−405.

(36) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Orgnometallics* **1985**, *4*, 83−91.

(37) Grillone, N. D.; Palmisano, L. *Transition Met. Chem.* **1989**, *14*, 81−89.

(38) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagn, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

The calculations were carried out with the SHELXL-97 program[39] using the integrated system WINGX(1.63).[40] Molecular view was realized with the help of ORTEP.[41] Fractional atomic coordinates and anisotropic thermal parameters for non hydrogen atoms and atomic coordinates for H atoms have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge, on application to the Director, CCDC, 12 Union Road Cambridge CB2 IE2, UK.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM020130B

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[39] Sheldrick, G. M. *SHELX97*, *Programs for Crystal Structure Analysis (Release 97-2)*; Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

[40] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

[41] (a) Burnett, M. N.; Johnson, C. K. *ORTEP-III, Report ORNL-6895*; Oak Ridge National Laboratory: Oak Ridge, TN, 1996. (b) Farrugia, L. J. *ORTEP3 for Windows*. *J. Appl. Crystallogr.* **1997**, *30*, 565.