

STUDIES OF CHELATION

IV*. STERIC INFLUENCES ON THE CHELATION OF DITERTIARY PHOSPHINE COMPLEXES OF GROUP VI METAL CARBONYLS

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Summary

The preparation of the complexes $[M(CO)_n(dcpe)]$ [$M = Cr, Mo, W; n = 4, 5$; $dcpe$ is $((cyclo-C_6H_{11})_2PCH_2)_2$] is reported. Attempts to prepare $[M(CO)_2(dcpe)_2]$ by many different methods gave only *cis*- $[M(CO)_4(dcpe)]$ and $[M(CO)_5(dcpe)]$. Heating *cis*- $[M(CO)_4(dcpe)]$ with $(Me_2PCH_2)_2(dmpe)$ gives *cis*- $[M(CO)_2(dmpe)_2]$ only. These observations are explained in terms of unfavourable intramolecular non-bonded interactions between substituents at phosphorus. The rate of chelation of $[M(CO)_5(dcpe)]$ to give *cis*- $[M(CO)_4(dcpe)]$ has been measured at various temperatures in the range 360–420 K. The activation parameters indicate the dominance of a dissociative process leading to the observed steric acceleration in the chelation step. The rate of chelation is correlated satisfactorily with the ligand cone angle; the operation of an apparent saturation effect is noted.

Introduction

The consequences of steric influences upon the chemical reactivity and the physical properties of coordination compounds, particularly of organo-transition-metal complexes are increasingly recognised as important [1]. A comparison of the complexes formed by tricyclohexylphosphine, PCy_3 , with those formed by other tertiary n-alkyl phosphines would indicate that in many instances the formation and reactions of such complexes appear to correlate better with the steric requirement of the cyclohexyl groups than with the basicity of the phosphine as measured by the pK_a value [2]. Recently an empirical index of steric strain, the ligand cone angle (LCA), has been defined [3] as the angle made by the tangent to the ligand with the metal—phosphorus axis. A number of studies

* For part III see ref. 15.

have shown a linear correlation between the LCA's of phosphines and the rates [4] or equilibrium constants [5] of processes in which metal complexes of those phosphines are involved.

We have sought to substantiate our earlier finding [6] that the rate of chelation of a ditertiary phosphine $R_2PCH_2CH_2PR_2$ in complexes of the type $[M(CO)_5(PR_2C_2H_4PR_2)]$ to give *cis*- $[M(CO)_4(PR_2C_2H_4PR_2)]$ is apparently subject to slight steric acceleration; thus, when $R = Ph$ (dpe), chelation is faster than when $R = Me$ (dmpe) independent of whether $M = Cr$ or Mo . To this end we have examined complexes formed by ethylenebis(dicyclohexylphosphine), $R = cyclo-C_6H_{11}$ (dcpe). We also report the results of unsuccessful attempts to prepare complexes of the type $[M(CO)_2(dcpe)_2]$ ($M = Cr, Mo, W$).

Results and discussion

The reaction between $Et_4N[M(CO)_5I]$ ($M = Cr, Mo$) and dcpe in the presence of Et_3OBF_4 in methylene chloride solution gave the complex $[M(CO)_5(dcpe)]$ in the form of bright yellow crystals. Yields (ca. 50%) were lower than usual ($> 90\%$) by this method [7], both because of the ease with which conversion to the chelated *cis*- $[M(CO)_4(dcpe)]$ occurred in solution even at 273 K and because of the relatively poor solubility of $[M(CO)_5(dcpe)]$ in ethyl ether. Characterisation of the pure complexes was straightforward and unexceptional.

The pale yellow chelate complexes *cis*- $[M(CO)_4(dcpe)]$ ($M = Cr, Mo, W$) were obtained in moderate (50–70%) yield simply by heating $M(CO)_6$ with dcpe (1/1) at 400–440 K for 10–30 h (temperature and duration depend upon M) in an evacuated sealed tube [8]. Repeated attempts to prepare the tetracarbonyl complexes by heating $Cr(CO)_6$ with dcpe in ethanol solution in the presence of a small amount of $NaBH_4$ [9] were unsuccessful. The monomeric, high melting solid complexes were characterised in the usual way and no features of particular note were found. Whereas we find that dcpe can effect *cis* disubstitution of $M(CO)_6$, PCy_3 reacts with $M(CO)_6$ to give *trans*- $[M(CO)_4(PCy_3)_2]$ as the only disubstituted product [10a]*. This reflects not only the fact that the two donor atoms are linked in dcpe, since a polymeric $\{trans-[M(CO)_4(dcpe)]\}_n$ could in principle have been formed, but also the fact that the steric requirement, as indicated by the LCA, of dcpe (147°) is less than that of PCy_3 (179°), and similar to that of PPh_3 (145°) which forms *cis*- $[M(CO)_4(PPh_3)_2]$ complexes.

Compounds of the type *cis*- $[M(CO)_2(LL)_2]$ ($LL = dmpe, dpe$) are formed easily [11] by heating $M(CO)_6$ ($M = Mo, W$) with LL (1/2) at ca. 480 K for 18 h, or by ultraviolet irradiation of $M(CO)_6$ ($M = Cr, Mo$) with LL (1/2) in MeCN solution or by treatment of $[W(CO)_2(\eta-C_6H_8)_2]$ with LL (1/2) in boiling hexane. It has also been shown that *cis*- $[M(CO)_4LL]$ reacts with a further mole of LL to give $[M(CO)_2(LL)_2]$ and that the binuclear complex $[M_2(CO)_6(LL)_3]$ is an intermediate in this process. The binuclear complexes can be formed directly from the reaction between either $[M(CO)_3(\eta-C_7H_8)]$ or $[M(CO)_3(MeCN)_3]$ and LL . We have tried all of these approaches to the synthesis of $M(CO)_2(dcpe)_2$ ($M = Mo, W$) without success.

* Compare this behaviour with that of PMe_3 [10b].

When $\text{Mo}(\text{CO})_6$ and dcpe (1/2) were heated even at 520 K for 30 h the sole product was $\text{cis-}[\text{Mo}(\text{CO})_4(\text{dcpe})]$. Irradiation of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$) and dcpe (1/2) in acetonitrile solution at 280 K with a medium pressure mercury discharge lamp, even after 70 h, gave only $\text{cis-}[\text{M}(\text{CO})_4(\text{dcpe})]$ and a small amount of $[\text{W}(\text{CO})_5(\text{dcpe})]$. Irradiation of pure $\text{cis-}[\text{M}(\text{CO})_4(\text{dcpe})]$ and dcpe (1/1) under similar conditions showed no evidence of change after 20 h and the starting materials could be recovered quantitatively. In the same way, when $[\text{W}(\text{CO})_3(\text{MeCN})_3]$ and dcpe (1/2) were heated (470 K, 18 h) in vacuo the products were $[\text{W}(\text{CO})_4(\text{dcpe})]$ together with $[\text{W}(\text{CO})_5(\text{dcpe})]$ and $\text{W}(\text{CO})_6$. No trace of $[\text{W}_2(\text{CO})_6(\text{dcpe})_3]$ was observed even by infrared spectroscopy of the reaction mixture before elaboration. This result is similar to the recent observation [12] that when $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{H}_5\text{Me})]$ or $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_8)]$ are treated with PCy_3 in diglyme, the only complex produced is $\text{trans-}[\text{M}(\text{CO})_4(\text{PCy}_3)_2]$; attempts to obtain $[\text{M}(\text{CO})_3(\text{PCy}_3)_3]$ were unsuccessful. An indication of the contrast between dcpe and dmpe in these systems was given by the finding that when $\text{cis-}[\text{Mo}(\text{CO})_4(\text{dcpe})]$ and dmpe were heated together (450 K, 20 h) the only molybdenum-containing product was $\text{cis-}[\text{Mo}(\text{CO})_2(\text{dmpe})_2]$ which was characterized by infrared and mass spectra and conversion to $[\text{Mo}(\text{CO})_2(\text{dmpe})_2\text{H}]\text{HCl}_2$ [13]. No evidence was found for the formation of $[\text{Mo}(\text{CO})_2(\text{dcpe})(\text{dmpe})]$. This inability to prepare any of the $[\text{M}(\text{CO})_2(\text{dcpe})_2]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes by the methods described is interesting because we believe it demonstrates convincingly the important influence of steric constraints in these systems. Models show that the interference of non-bonded cis-PCy_2 groups is strong in both of the possible isomeric structures of $[\text{M}(\text{CO})_2(\text{dcpe})_2]$.

Chelation of $[\text{M}(\text{CO})_5(\text{dcpe})]$

The infrared spectrometric method used in previous work [6,7] was adopted. Solutions of the complex in *n*-nonane were heated in a closed vessel and the progress of the chelation was monitored by the decrease in absorbance of the $\nu(\text{CO})$ *E* mode of $[\text{M}(\text{CO})_5(\text{dcpe})]$ and the corresponding increase in absorbance of the $\nu(\text{CO})\text{B}_2$ mode of $\text{cis-}[\text{M}(\text{CO})_4(\text{dcpe})]$. Rate constants and activation parameters were evaluated using a computer. The results of at least four sets of measurements at each temperature are presented in Table 1.

The conclusions of our previous work are substantiated. For any given ligand, the rate of chelation at molybdenum is greater than that at chromium; for any particular metal the rate of chelation increases in the order $\text{LL} = \text{dmpe} > \text{dpe} > \text{dcpe}$. This is further emphasised by a plot of rate constant for chelation against the LCA of the ligand (Fig. 1). Steric acceleration is observed unambiguously for molybdenum, indicating that the dissociative process is the dominant path of chelation. The fact that the plot is not linear for chromium may suggest that, as a result of the smaller size of chromium, the extent of steric acceleration is limited and that the associative contribution to a concerted process increases in importance when steric hinderance is very great. In general, however, the results show the greater importance of bond breaking relative to bond making in this type of substitution. Our results are comparable to those found [14] in the carbonylation of $\text{cis-}[\text{M}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NR}_2)]$ ($\text{M} = \text{Cr}, \text{Mo}$; $\text{R} = \text{H}, \text{Me}, \text{Et}$) in acid where the rate of ring closure (k_{-1}) of the coordinatively unsaturated intermediate is not strongly dependent of the size of R. The

TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS

Rate constants for chelation of $M(CO)_5(dcpe)$ ($k \times 10^5 s^{-1}$)			
Temp (K)	M = Mo	Temp. (K)	M = Cr
363	4.5	393	18.5
373	14.5	403	61.0
383	49.5	413	168.0
393	132.0		

Activation parameters for chelation of $M(CO)_5LL$			
M	LL	$\Delta H/kJ mol^{-1}$	$\Delta S/JK^{-1} mol^{-1}$
Cr	dmpe	132	6
	dpe	135	27
	dcpe	147	46
Mo	dmpe	118	-7
	dpe	120	14
	dcpe	132	34

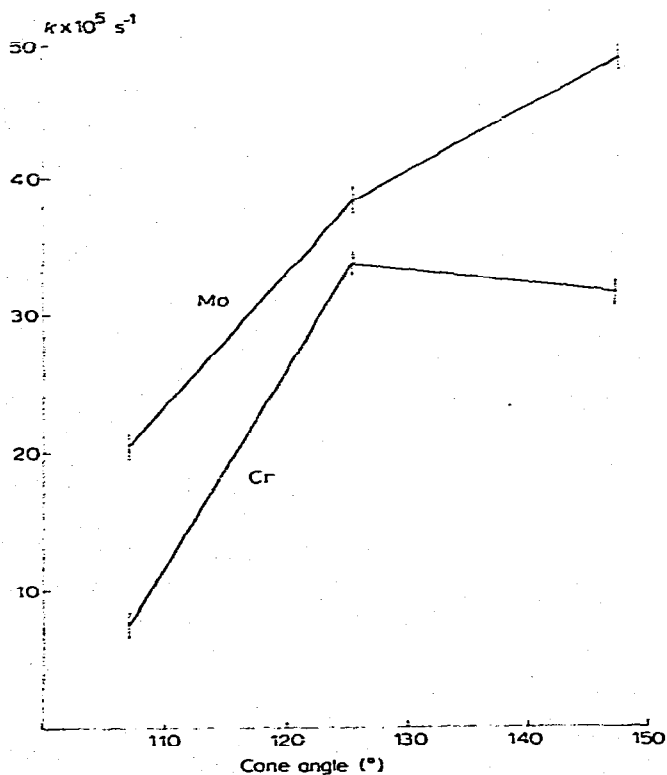


Fig. 1. Plot of rate of chelation ($k \times 10^5 s^{-1}$) vs. ligand cone angle ($^\circ$) for $[M(CO)_5(dcpe)]$ M = Cr at 397 K. M = Mo at 383 K.

fine balance between the associative and dissociative paths in chelation processes of this type is shown by the fact that the rate of dissecondary sulphide chelation onto $[\text{Mo}(\text{CO})_5(\text{RSC}_2\text{H}_4\text{SR})]$ is subject to slight but significant steric retardation [15].

The LCA's used here are those estimated [5] for phosphorus complexes of nickel, assuming a value for the Ni(O)—P bond length of 228 pm. It is a simple matter to show that the slight increase in M(O)—P bond length [Cr(O)—P av. 237 pm [16]; Mo(O)—P av. 252 pm [17]] and the slight reduction in the ligand bite angle (from ca. 84° to ca. 76°) in chelating ditertiary phosphine complexes on proceeding from right to left along the *d*-transition metals [18], has only a small and negligible effect upon the LCA. Thus the LCA of dmpe, which is 107° on nickel, falls to 102° on molybdenum. The corresponding values for dcpe are 147(Ni) and 144(Mo). We have therefore retained Tolman's values to avoid possible confusion.

Experimental

Materials and methods were generally the same as in previous work [6]. The ligand dcpe was prepared by the route suggested by Issleib [19]. In the preparation of PHCy_2 the excess LiAlH_4 , remaining after reduction of $\text{Cy}_2\text{P}(\text{O})\text{Cl}$, was decomposed by the addition of aqueous sodium/potassium tartarate (10% w/v). Pure dicyclohexylphosphine (50 g, 0.25 mol) and 1,2-dibromoethane (27.2 g, 0.137 mol) were heated together at reflux until solidification occurred (453 K oil bath, 2.5 h). After cooling to room temperature, absolute ethanol (600 cm^3) was added to the mixture which was then heated at reflux until a clear solution was obtained. Solid sodium hydroxide (16 g, 0.53 mol) was added in portions to the refluxing solution to render the solution alkaline (pH paper). The sodium bromide was removed by filtration from the hot solution. The filtrate was stored at 260 K, producing colourless crystals of dcpe (67 g, 0.16 mol, 70%) characterised by microanalysis, m.p., IR, NMR and mass spectrometry, and formation of two derivatives as follows:

(a) Hydrogen peroxide (1 cm^3 , 100 vol %) was added to a stirred suspension of dcpe (0.5 g, 1.19 mmol) in ice-cold ethanol. The resulting clear solution was stirred for 0.5 h. The product was purified by reprecipitation (ether) and was shown to be ethylene bis(dicyclohexylphosphine oxide) (52%) m.p. 465-468 K. (Found: C, 69.2; H, 10.0. $\text{C}_{26}\text{H}_{48}\text{O}_2\text{P}_2$ calcd.: C, 68.7; H, 10.6%). *m/e* (*I*, %) 454 (10, M^+), 453 (14), 371 (37), 370 (100), 289 (42), 288 (100), 241 (19), 240 (91) ν_{max} 1210 vs cm^{-1} (P=O).

(b) Dcpe (0.93 g, 2.20 mmol) was added to a stirred solution of Me_3OBF_4 (0.67 g, 4.5 mmol) in acetonitrile (25 cm^3). The solvent was removed and the residue dissolved in CH_2Cl_2 . Addition of ether precipitated a white solid which was purified by reprecipitation to give ethylene bis(dicyclohexylmethylphosphonium) ditetrafluoroborate (51%) m.p. 515-519 K. (Found: C, 53.5; H, 8.9. $\text{C}_{28}\text{H}_{54}\text{B}_2\text{F}_8\text{P}_2$ calcd.: C, 53.7; H, 8.6%).

The complex $[\text{Cr}(\text{CO})_5(\text{dcpe})]$ was prepared from $[\text{Et}_4\text{N}(\text{CO})_5\text{I}]$ and obtained as bright yellow crystals (50%). (Found: C, 56.4; H, 7.9. $\text{C}_{31}\text{H}_{48}\text{CrO}_5\text{P}_2$ calcd.: C, 60.5; H, 7.8%.) ν_{max} 2060m, 1942 m (sh), 1943 s (hexane), 2062 m, 1930 s (br) (CH_2Cl_2) cm^{-1} . *m/e* (*I*, %) 586 (23, $M - \text{CO}$), 558 (0), 520 (0), 492 (38),

464 (100). In a similar way, $[\text{Mo}(\text{CO})_5(\text{dcpe})]$ was made from $[\text{Et}_4\text{NMo}(\text{CO})_5\text{I}]$ and obtained as yellow crystals (46%) (Found: C, 54.9; H, 7.6. $\text{C}_{31}\text{H}_{48}\text{MoO}_5\text{P}_2$ calcd.: C, 56.5; H, 7.4%.) ν_{max} 2070 m, 1959 m (sh), 1940 vs (hexane), 2068 m, 1938 s (br) (CH_2Cl_2) cm^{-1} . m/e (I, %) 660 (0, M^+), 632 (34), 604 (46), 576 (86), 548 (200), 520 (100).

Preparation of $M(\text{CO})_4(\text{dcpe})$

The metal hexacarbonyl (2 mmol) and dcpe (2 mmol) were sealed in an evacuated Carius tube and heated (Cr, 403 K, 12 h; Mo, 433 K, 20 h; W, 433 K, 24 h). Addition of methylene chloride (25 cm^3) to the bright yellow solid product, filtration and then addition of ether precipitated the complex which was purified by reprecipitation. *cis*- $[\text{Cr}(\text{CO})_4(\text{dcpe})]$ (48% yield) m.p. 513-515 K (dec). (Found: C, 61.2; H, 8.3; Cr, 9.0; P, 10.6. $\text{C}_{30}\text{H}_{48}\text{CrO}_4\text{P}_2$ calcd.: C, 61.4; H, 8.2; Cr, 8.9; P, 10.6%.) ν_{max} 2002 s, 1912 s, 1890 vs (sh), 1886 vs (hexane), 1996 vs, 1882 m, 1874 vs, 1866 vs (sh) (CH_2Cl_2) cm^{-1} . *cis*- $[\text{Mo}(\text{CO})_4(\text{dcpe})]$ (70% yield) m.p. 511-513 K (dec). (Found: C, 57.1; H, 7.7; Mo, 15.2; P, 9.8. $\text{C}_{30}\text{H}_{48}\text{MoO}_4\text{P}_2$ calcd.: C, 57.1; H, 7.6; Mo, 15.2; P, 9.8%.) ν_{max} 2016 s, 1922 s, 1896 vs (hexane), 2010 s, 1906 s, 1886 vs, 1870 vs (sh) (CH_2Cl_2) cm^{-1} . m/e (I, %) 632 (34, M^+), 604 (46), 576 (86), 548 (200), 520 (100). *cis*- $[\text{W}(\text{CO})_4(\text{dcpe})]$ (68% yield) m.p. 518-521 K (dec). (Found: C, 49.8; H, 6.7; P, 8.7; W, 25.6. $\text{C}_{30}\text{H}_{48}\text{O}_4\text{P}_2\text{W}$ calcd.: C, 50.1; H, 6.7; P 8.6; W 25.6%.) ν_{max} 2010 s, 1912 s, 1890 vs. 1884 vs (hexane), 2018 s, 1906 s, 1890 vs, 1878 s (sh) (CH_2Cl_2) cm^{-1} . m/e (I, %) 718 (133, M^+), 680 (665), 652 (300), 624 (475), 596 (100).

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