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Substituted metal carbonyls
Part 19. Synthesis and XPS characterisation of dimanganese(0) carbonyl phosphites

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Abstract

Oxidative decarbonylation of $Mn_2(CO)_{10}$ by amine oxide in the presence of phosphites $P(OR)_3$ (R = Me, Et, Ph, CH_2CF_3, CH_2CH_2Cl) led to good yields of $Mn_2(CO)_9[P(OR)_3]$. Coordination of the phosphite and its influence of the manganese centres have been studied by P(2p) and Mn(2p) X-ray photoelectron spectroscopy.

Introduction

The reminiscence of phosphites to carbonyls and phosphines has prompted an extensive study of the electronic and chemical properties of the former in many substituted metal carbonyls [1]. It is acknowledged that by tailoring the electronic properties of the substituents on $P(OR)_3$, one can even synthesise the phosphite analogues of some binary carbonyls; a well known example being the synthesis of $Re_2(P(OMe)_3)_{10}$ [2]. While a host of phosphine substituted manganese carbonyls is known [3], to date our knowledge on the dinuclear phosphite complexes is mainly confined to $Mn_2(CO)_9[P(OR)_3]$ (R = Me [4], Ph [5]) and $Mn_2(CO)_8[P(OR)_3]_2$ (R = Me [6], Et [7], Ph [8]). Using the proven amine oxide initiated decarbonylative technique [9], we herein report the synthesis of $Mn_2(CO)_9[P(OR)_3]$ (R = Me, Et, Ph, $-CH_2CH_2Cl$, $-CH_2CF_3$) and explore their influence on the metal sphere through X-ray photoelectron spectroscopy (XPS).

Experimental

General procedures

All reactions were performed under pure dry argon using standard Schlenk techniques. Chemical reagents were supplied from commercial sources and were used without further purification. Precoated silica plates of layer thickness 0.25 mm were obtained from Merck. Solvents were reagent grade and were freshly dried and distilled under N_2 and purged with argon before use. Proton NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.55 MHz using $(CH_3)_4Si$ as internal standard. Phosphorus-31 NMR spectra were recorded on the same instrument at 36.23 MHz. Chemical shifts are reported in ppm to the high frequency of external 85% H_3PO_4. IR spectra were recorded as hexane solutions on a Perkin-Elmer 1310 or FT-IR Perkin-Elmer 1710 spectrometer. Elemental analyses were performed by the Analytical Service of this department. Core level XPS spectra were obtained on VG ESCA/SIMSLAB MK II spectrometer using Mg Kα radiation, operating on a fixed retardation of 40 and covered the energy region for all the elements contained. The sample in powder form was sprinkled onto a double-sided Scotch tape mounted onto a standard VG holder. The binding energies were referenced to the hydrocarbon component in the C_{1s} envelope defined at 285.0 eV to compensate for surface charging. The b.e. of each core ionisation peak was determined from a symmetric curve fit of the band and is estimated to have an uncertainty of ±0.3 eV. Surface atomic stoichiometric ratios were measured from peak area ratios corrected with appropriate experimentally determined sensitivity factors. No strenuous effort was made to resolve the P(2p) sub-levels. However, literature data [10] suggested that $2p_{1/2}$ is rarely registered whilst $2p_{3/2}$ is commonly recorded and reported for phosphine complexes. For the Mn

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spectrum, the peaks recorded correspond to the low energy Mn($2p_{3/2}$) bands [11].

Preparations

The preparation of $Mn_2(CO)_9[P(OCH_2CH_2Cl)_3]$ represents a typical procedure for the monosubstituted dimanganese complexes and is described here.

$Mn_2(CO)_{10}$ (0.398 g; 1.02 mmol) and $(CH_3)_3NO \cdot 2H_2O$ (0.114 g; 1.02 mmol) were dissolved in thf (50 ml) to give an orange solution to which was added $P(OCH_2CH_2Cl)_3$ (0.20 ml; 0.98 mmol). The resultant orange mixture was stirred at r.t. for *c.* 4 h, after which the solvent was removed under vacuum. The residue thus obtained was extracted with a minimum quantity of CH_2Cl_2 to give an orange–yellow solution which was applied to silica TLC plates. Elution with hexane/CH_2Cl_2 (4:1) solution led to the isolation of $Mn_2(CO)_9[P(OCH_2CH_2Cl)_3]$ which was further purified by recrystallisation from hexane to give yellow microcrystals (0.150 g; 23.3%). *Anal.* Found: C, 28.5; H, 1.8; P, 5.0; Mn, 15.9. Calc. for $C_{15}H_{12}Cl_3Mn_2O_{12}P$: C, 28.5; H, 1.9; P, 4.9; Mn, 17.4%. ν(CO): 2090(w), 2020(s), 1995(vs), 1975(m), 1945(m). ^{1}H NMR: δ 4.32(dt, $-OCH_2-$), 3.77(t, $-CH_2Cl$); J(HH) = 5.4 Hz, J(HP) = 3.4 Hz. ^{31}P NMR: δ −15.8(br).

$Mn_2(CO)_9[P(OCH_3)_3]$ (0.254 g; 51.2% based on $Mn_2(CO)_{10}$ (0.398 g)). *Anal.* Found: C, 29.6; H, 1.7; P, 5.8; Mn, 22.8. Calc. for $C_{12}H_9Mn_2O_{12}P$: C, 29.6; H, 1.9; P, 6.4; Mn, 22.6%. ν(CO): 2100(w), 2020(s), 2000(vs), 1975(m), 1950(m). ^{1}H NMR: δ 3.75(d, CH_3), J(HP) = 11.5 Hz. ^{31}P NMR: δ −12.0(br).

$Mn_2(CO)_9[P(OC_2H_5)_3]$ (0.234 g; 43.0% based on $Mn_2(CO)_{10}$ (0.402 g)). *Anal.* Found: C, 34.9; H, 2.9; P, 4.5; Mn, 18.6. Calc. for $C_{15}H_{15}Mn_2O_{12}P$: C, 34.1; H, 2.8; P, 5.9; Mn, 20.8%. ν(CO): 2080(w), 2000(s), 1990(vs), 1970(m), 1945(m).

$Mn_2(CO)_9[P(OC_6H_5)_3]$ (0.139 g; 39.9% based on $Mn_2(CO)_{10}$ (0.202 g)). *Anal.* Found: C, 48.4; H, 2.1; P, 4.5; Mn, 15.9. Calc. for $C_{27}H_{15}Mn_2O_{12}P$: C, 48.2; H, 2.2; P, 4.6; Mn, 16.3%. ν(CO): 2090(w), 2020(s), 1995(vs), 1970(s), 1950(m). ^{1}H NMR: δ 7.29–7.48(m, Ph). ^{31}P NMR: δ 20.2(br).

$Mn_2(CO)_9[P(OCH_2CF_3)_3]$ (0.091 g; 25.2% based on $Mn_2(CO)_{10}$ (0.204 g)). *Anal.* Found: C, 26.6; H, 0.8; P, 4.3; Mn, 16.7. Calc. for $C_{15}H_6F_9Mn_2O_{12}P$: C, 26.1; H, 0.9; P, 4.5; Mn, 15.9%. ν(CO): 2100(w), 2030(s), 2000(vs), 1990(m), 1960(m). ^{1}H NMR: δ 4.06(br)(d, CH_2).

$Mn_2(CO)_9[P(C_6H_5)_3]$ (0.058 g; 17.9% based on $Mn_2(CO)_{10}$ (0.203 g)). *Anal.* Found: C, 53.5; H, 2.8; P, 4.6; Mn, 15.5. Calc. for $C_{27}H_{15}Mn_2O_9P$: C, 51.9; H, 2.4; P, 5.0; Mn, 17.6%. ν(CO): 2085(w), 2010(sh), 1996(s), 1973(m), 1940(m).

For the preparation of the disubstituted complexes, two molar equivalents of TMNO and $P(OPh)_3$ or PPh_3 are used.

$Mn_2(CO)_8[P(OC_6H_5)_3]_2$ (0.031 g; 6.3% based on $Mn_2(CO)_{10}$ (0.200 g)). ν(CO)(hexane): 1995(sh), 1984(s).

$Mn_2(CO)_8[P(C_6H_5)_3]_2$ (0.017 g; 3.8% based on $Mn_2(CO)_{10}$ (0.203 g)). ν(CO)(hexane): 1980(w), 1952(m).

Results and discussion

Phosphite substitution of $Mn_2(CO)_{10}$, the occurrence of which in refluxing xylene has been reported, is found to be negligibly slow in boiling thf. Disubstitution is generally observed under photo- and thermolytic conditions in many literature reports [3]. However, in the presence of stoichiometric ratio of Me_3NO, ligand replacement occurs rapidly at r.t. to give *ax*-$Mn_2(CO)_9[P(OR)_3]$ (where R = Me, Et, Ph, CH_2CH_2Cl and CH_2CF_3) in which the integrity of the Mn–Mn bond is preserved. Only at a higher concentration of amine oxide and $P(OR)_3$ is the disubstituted species $Mn_2(CO)_8[P(OR)_3]_2$ formed in any isolable quantity. These oxygen migratory reactions from the amine oxide to the carbonyl carbon have been recently reviewed [12]. We have no evidence that TMNO could initiate the rupture of the Mn–Mn bond in the course of the reaction. All the novel complexes are spectroscopically characterised though the ^{31}P NMR spectra were unsatisfactory due to quadrupolar coupling (^{55}Mn, $I = 5/2$, 100%). Either very broad or no apparent ^{31}P signal is observed for these monosubstituted complexes. The IR spectral characteristic of some mono- [13] and disubstituted [14] dinuclear manganese carbonyls have been reported. Most of these complexes also readily decompose in solution thus rendering their identification difficult. It is in this context that the Mn(2p) and P(2p) XPS analysis plays a more diagnostic role in their characterisations. A summary of the XPS data is listed in Table 1. The phosphine analogue $Mn_2(CO)_9(PPh_3)$, $Mn_2(CO)_{10}$, and $(OC)_9Mn_2(\mu$-dppf$)Mn_2(CO)_9$ [15] are included for comparative purpose. Similarly, disubstituted complexes $Mn_2(CO)_8(P)_2$ (P = PPh_3 and $P(OPh)_3$) [16] were also synthesised and studied.

As expected the binding energies (b.e.s) of P(2p) increase slightly but steadily as the phosphite substituent becomes increasingly electronegative, thus reflecting the decreasing σ-donation and increasing π-acidity of the ligand. Among the monophosphite complexes, a disparity of 0.9 eV is found between the methyl and phenyl phosphites, and lower for other phosphites. Such small variation is consistent with those observed for some nickel [17] and molybdenum [18] phosphite complexes. However, if the

TABLE 1. Molecular core binding energies (eV) of some phosphine and phosphite substituted manganese(0) carbonyls[a]

Complex	P(2p)	Mn(2p)
$Mn_2(CO)_9[P(OMe)_3]$	133.2(2.0)	640.8(1.8)
$Mn_2(CO)_9[P(OPh)_3]$	134.1(2.1)	641.3(1.9)
$Mn_2(CO)_8[P(OPh)_3]_2$	133.8(2.2)	640.9(2.3)
$Mn_2(CO)_9[P(OCH_2CH_2Cl)_3]$	133.3(2.1)	641.0(2.1)
$Mn_2(CO)_9[P(OCH_2CF_3)_3]$	133.4(2.0)	641.1(2.0)
$Mn_2(CO)_{10}$		642.3(3.9)
$Mn_2(CO)_9(PPh_3)$	131.7(2.4)	640.9(2.3)
$Mn_2(CO)_8(PPh_3)_2$	131.7(2.4)	640.9(2.2)
$[Mn_2(CO)_9]_2(\mu\text{-dppf})$	131.8(2.7)	641.2(2.8)

[a] Core level binding energies referenced to hydrocarbon peak at 285.0 eV; full-width half-maximum values are given in parentheses.

phosphite is replaced by phosphine, as exemplified in $Mn_2(CO)_9L$ ($L = P(OPh)_3$ and PPh_3), the much lower phosphorus contribution to σ^* of the M–P bond [19] and lower π backdonation of the latter enables the detection of a significant drop of 2.4 eV in the P(2p) b.e. Though these changes of electronic demand of the phosphite substituents are also reflected in the Mn(2p) b.e.s, the variations are however much less noticeable, with the phosphite complexes covering a narrow range of 640.8–641.3 eV. The phosphine complexes also lie within this region. Such insensitivity of the shift to the chemical environment is however not unexpected in view of the fairly narrow range of shift values found in a similar series of mono- and dinuclear Mn(0) and Mn(I) species [20]. The significantly lower Mn(2p) b.e.s in these complexes compared to that of their parent $Mn_2(CO)_{10}$ are however justified by the superior ability for the carbonyl ligand to dissipate charges away from the metal centre, even when compared with ligands which are notoriously acidic, e.g. $P(OPh)_3$ and $P(OCH_2CF_3)_3$. Noteworthy is that the two chemically non-equivalent metal sites in these mono-substituted dimanganese products $(OC)_5Mn–Mn(CO)_4(P)$ are not differentiable in the Mn(2p) spectra. Comparison of their band shapes, breadth and shifts with those of complexes with equivalent metal sites, e.g. $Mn_2(CO)_{10}$, $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_8[P(OPh)_3]_2$ reveals no further band broadening. While we attribute this to an intrinsic insensitivity of the Mn(2p) core ionisation energies to changes in a distant neighbouring group, an efficient charge equilibration across the Mn–Mn bond, hence diminishing their electronic contrast, cannot be ruled out. A similar observation is noted on the Mn(2p) peak in a cluster molecule $(OC)_9Mn_2(\mu\text{-dppf})Mn_2(CO)_9$ which consists of a singly bridging dppf unit spanning across two otherwise unlinked metal–metal bonded $Mn_2(CO)_9$ entities [21]. Both the P(2p) and Mn(2p) b.e. data suggest its similarity to $Mn_2(CO)_9(PPh_3)$ whilst the two Mn(2p) sites are still indistinguishable in the XPS spectra. Integration of the Mn and P peak areas in these complexes neatly indicate the statistical distribution of the nuclei in the molecules. A surface atomic stoichiometric ratio of 1:1 and 2:1 for Mn:P characterises the di- and monosubstituted derivatives, respectively. Apart from this integration ratio, spectra of $Mn_2(CO)_9(PPh_3)$ and $Mn_2(CO)_8(PPh_3)_2$ are barely distinguishable whereas for their $P(OPh)_3$ analogues, a slight depression of 0.4 eV in the Mn(2p) b.e. is accompanied by a second axial substitution, which indicates a slight but detectable increase of charge density on the metals when the second carbonyl is replaced.

The present study, though still plagued with peak broadening due possibly to the generation of very short-lived excited states, encourages the use of XPS in the characterisation of organometallic compounds in their solid state. While the subtle changes of metal binding energy reveal little of the electronic and structural environment of the complexes, the information derived from ligand group shift [22] has been proved to be invaluable, particularly for paramagnetic and quadrupolar nuclei where the conventional NMR analysis is elusive.

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