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New organometallic complexes of buckminsterfullerene having π-bonded nickel, palladium, or platinum with triorganophosphite ligands, and their characterisation

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Abstract

We have prepared a series of novel π-complexes of fullerene C_{60} of the types $[C_{60}\{M(P(OR)_3)_2\}_n]$, (M = Ni, Pd, or Pt; R = Ph, Bu, or Et; $n = 1$ or 2). The compounds have been characterised by mass spectrometry, electronic spectroscopy and proton, carbon, and phosphorus NMR spectroscopy. The sensitivity of these compounds to air increases greatly in the series Pt < Pd ≪ Ni. Unlike analogous phosphine derivatives, the phosphite species do not readily form complexes with more than two metal atoms attached to the fullerene cage. In contrast with many π-bonded fullerene derivatives, most of the compounds show molecular ions in the FAB mass spectrum.

Keywords: Nickel; Palladium; Platinum; Fullerene; C_{60}; Metal–fullerene complex

1. Introduction

Among the earliest reported organometallic compounds of fullerene-60 were π-complexes of Ni, Pd, or Pt phosphine derivatives [1]. Subsequently numerous reports have described π-complexes of these and other metals complexed with phosphines or with a combination of phosphines and other ligands [2–5]. Since it was established that the C_{60} cage is electron poor in character, and has effectively isolated double bonds, Group 10 phosphine complexes appeared to be promising reagents for the preparation of π-bonded derivatives. Furthermore, it was demonstrated that up to six such metal units could be attached in an octahedral array around the C_{60} cage, without any significant reduction in the complexing ability of the cage upon addition of each metal fragment. As might be expected from these facts, it appears that the electronic effects of metal binding do not extend in the cage substantially beyond the ligated C-atoms [6].

Except for two incompletely characterised compounds, one each of Pd [6] and Pt [7], and mention of a Ni compound [8], there have been no reports of triorganophosphite metal adducts. We now report on the synthesis and characterisation of a series of fullerene complexes having Ni, Pd, or Pt bound to triorganophosphites.

2. Results and discussion

Addition of a solution of the metal phosphite complex in toluene to one of C_{60} also in toluene [followed by heating to ca. 50–60°C in the case of the nickel species] afforded the adducts as deep-green solutions almost immediately (Pd or Pt), or when the temperature reached ca. 50°C (Ni). The compounds may be isolated by sequential (i) removal of solvent under vacuum, (ii) dissolution of the by-product (uncomplexed phosphite) in cold methanol (in which the adducts are generally insoluble or only sparingly soluble), and extraction of the products into THF, in which C_{60} is virtually insoluble.

$$C_{60} + n[M\{P(OR)_3\}_4] \longrightarrow C_{60}[M\{P(OR)_3\}_2] + 2P(OR)_3 \qquad (1)$$

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The solid materials can be obtained by removal of solvent under vacuum, or by addition of ethanol to the THF solution. When the THF is allowed to evaporate slowly from such solutions in THF/ethanol microcrystalline products result, which, however, have so far proved unsuitable for single crystal X-ray analysis. Solutions of the adducts are dark green in all the solvents examined (THF, ether, CS_2, toluene, hexane, benzene, or weakly, in ethanol), though there is a red tinge in transmitted light.

Whereas the nickel compounds, either in solution or as solids, are rapidly decomposed in the presence of oxygen, the palladium and platinum species are air stable as solids, and only decompose slowly (weeks for Pt) in solution. They all have reasonable thermal stability, surviving in refluxing toluene for extended periods. In all these properties the compounds appear to be similar to the analogous phosphine compounds.

In contrast to the compounds having phosphine ligands, it did not prove possible to isolate compounds having more than two metal centres attached to a C_{60} cage under any of the conditions studied (or those employed for the synthesis of higher derivatives of the phosphine ligated species [1b]), nor was there any evidence in solution for the formation of such adducts in solution. (A referee suggested that we examine the mass spectra of the crude materials for higher adducts. These show no evidence for the formation of adducts with more than two metals (though we cannot of course exclude the possibility that such adducts do not survive the ionisation conditions intact), in agreement with our original HPLC data.) Addition of a substantial excess (ca. 8–10 fold) of the metal phosphite complex (which for phosphine analogues readily affords the orange or red solutions of the hexa-adducts) causes a deepening of the green solution, which is attributable to the formation of *bis* adducts, but no evidence could be obtained for the formation of complexes having more than two metal centres.

Spectroscopic and mass spectrometric data are presented in Table 1. In all cases the peaks associated with the phosphite ligands are substantially shifted downfield from those for the free phosphite, and to a smaller, but reproducible, extent from those exhibited by the metal phosphite complexes. Full resolution of the ^{13}C spectra of the fullerene cage atoms has proved extremely difficult. However, in the case of compound (**I**), 10 of the expected 16 resonances were resolvable after accumulation of 138,000 FIDs. Of the remaining six expected resonances it is difficult to determine

Table 1

Compound	^1H NMR δ(ppm)	^{13}C NMR δ(ppm)		^{31}P NMR δ(ppm) [a]	UV/VIS (nm)	MS
(**1a**) $C_{60}[Pt\{P(OPh)_3\}_2]$	7.31 (complex multiplet)	147.8	144.1	132.3	589	M^+
		145.9	143.3		488	
		145.4	143.1		438	
		145.1	143.0		342	
		144.7	141.9			
		66.6 [b]				
		135.1	129.5			
		130.8	121.9			
(**1b**) $C_{60}[Pt\{P(OPh)_3\}_2]_2$				131.7	525	M^+
					427	
					(337)	
(**II**) $C_{60}[Pt\{P(OBu)_3\}_2]_n$	4.26(t)					M^+
	1.89(quin)	62.8	19.3	129.1		
	1.70(sext)	32.9	13.6			
	1.12(t)					
(**III**) $C_{60}[Pd\{P(OBu)_3\}_2]_n$	4.23	144(br)		145.4	591	$(M + 1)^+$
	1.65				($n = 1$)	
	1.40	64.3	19.1		489	
	0.87	32.9	13.6		(436)	
					(382)	
					343	
(**IV**) $C_{60}[Pd\{P(OEt)_3\}_2]_n$	4.29(quart)			144.7	526	$(M + 1)^+$
	1.18(t)				428	
					(336)	
(**V**) $C_{60}[Ni\{P(OBu)_3\}_2]_n$	4.29(t)					
	1.88(quin)					
	1.68(sext)					
	1.14(t)					

[a] Referenced with respect to 85% phosphoric acid (= 0). [b] Partially solvent-obscured.

whether they are undetectable because of accidental degeneracies, or owing to overlap with the (substantially stronger) peaks of the phosphite or of the solvent.

After exploration of several methods for obtaining the mass spectra of these species, (TOF, FAB, EI, CI) we found that satisfactory molecular ion data can be obtained for most of the compounds using a Xe atom FAB source. We are not aware of any other reported data for related π-complexes of fullerenes, including the closely related phosphine analogues. These spectra reveal, in addition to peaks for C_{60} apparently formed by breakdown in the spectrometer, ions for the species $[C_{60}\{M(P(OR)_3)_2\}_n]$, $n = 1$ or 2 in the case of *bis* adducts, or $n = 1$, for the monoadducts. In the case of **(II)** only the ion with $n = 2$ was detected, and it seems that the fragmentation does not include a significant pathway involving loss of a single $M\{P(OR)_3\}_2$ moiety. The reasons for this are not evident.

Analytical HPLC analysis (see Experimental details) of compounds **(Ia)**, **(Ib)**, and **(III)** demonstrates the presence of the *mono* and *bis* adducts. The comparatively high solubility of these adducts allowed the separation of high purity samples of compounds **(Ia)** and **(Ib)** in milligram quantities (Fig. 1). Elemental analysis of these compounds was attempted: For **(Ia)** Calc.: C, 75.05; H, 1.97; Found: C, 72.90; H, 2.49%; for **(Ib)** Calc.: C, 67.41; H, 2.57; Found: C, 68.16; H, 3.62%. These results are clearly of no diagnostic value, and such elemental analyses have been found to be highly variable for a range of metal fullerene compounds [9].

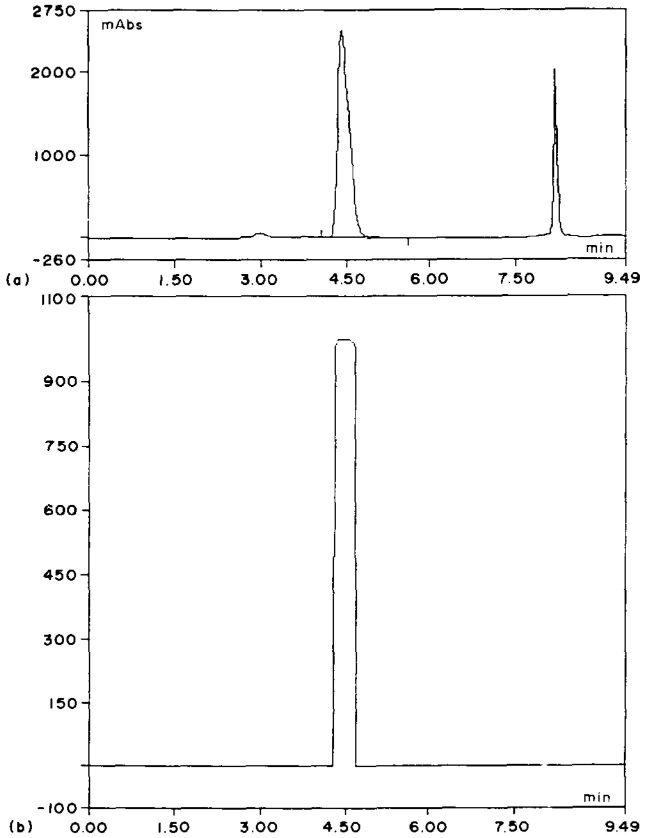

Fig. 1. (a) HPLC trace of compound **(Ia)** (peak 1) from experiment 3.2. with C_{60} reference; (b) peak purity profile of compound **(Ia)**.

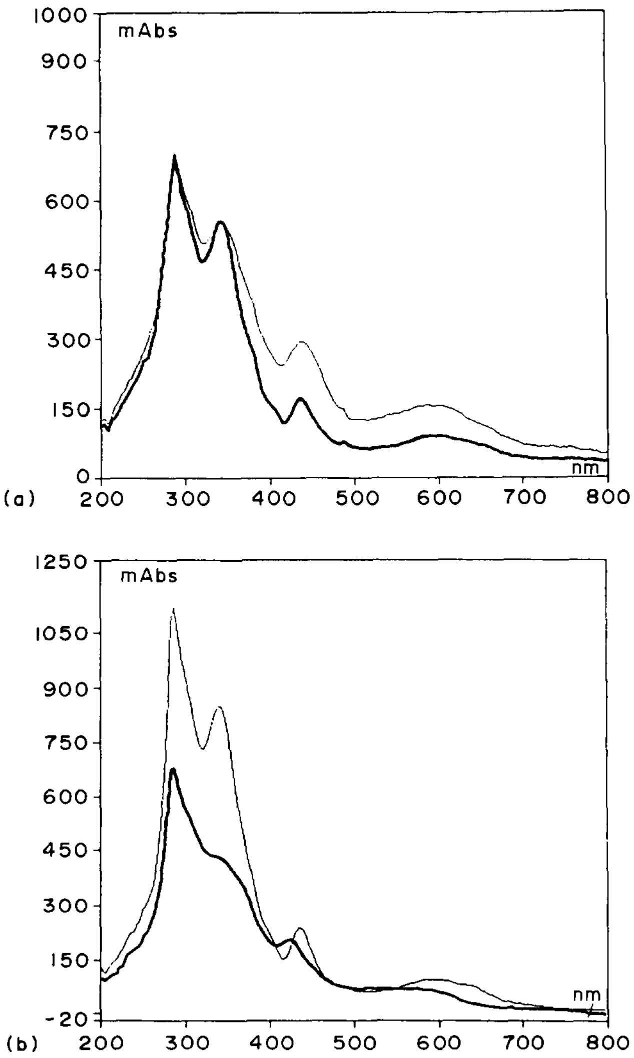

Fig. 2. Electronic spectra (nm) of (a) **(Ia)** and (lighter trace) **(III)** ($n = 1$); (b) **(Ib)** and (lighter trace) **(Ia)**.

UV data for solutions of the compounds are reported in Table 1. As expected, the spectra of the mono adducts are all extremely similar to each other, as are those of the *bis* adducts, though the two classes are readily distinguishable (Fig. 2).

We have also recorded the Raman and IR spectra of these compounds, and a detailed discussion of the results will be reported elsewhere.

3. Experimental details

Fullerenes were generated by resistive heating of graphite rods in a glass apparatus developed from the design described by Scrivens and Tour [10]. Prior to use, C_{60} was sonicated in ether and heated under vacuum at 250°C to remove volatile impurities. All manipulations were carried out under dried argon by use of Schlenk techniques and with strict exclusion of oxygen and moisture. All solvents were dried and degassed prior to use.

Metal phosphite precursors were prepared by the methods described in ref. [11]. Representative procedures are given below.

3.1. Synthesis of (V)

A solution of $[Ni\{P(OBu)_3\}_4]$ (0.479 g, 4.52×10^{-4} mol) in toluene (10 cm^3) was added by cannula to a stirred solution of C_{60} (54.2 mg, 7.53×10^{-5} mol) in toluene (50 cm^3). The mixture was stirred for 1 h then kept at 55°C for 24 h during which a dark-green colour developed. Solvent was removed under vacuum, and the product was washed in methanol (3 × 20 cm^3) and taken up in THF (50 cm^3). The extract was filtered and the THF removed under vacuum, to leave the product as a black powder. Because of trapping of toluene in the fullerene lattice, absolute yields could not be determined, but they were essentially quantitative (as estimated from amounts of recovered fullerene).

3.2. Synthesis of (I)

To a solution of C_{60} (72 mg, 1×10^{-4} mol) in toluene (50 cm^3) during 15 mins by cannula, solution of $[Pt\{P(OPh)_3\}_4]$ (144 mg 1×10^{-4} mol) (in toluene (15 cm^3)). The colour gradually changed from deep purple to green. The green solution was stirred overnight and the solvent removed under vacuum. Work-up was as above. The product was isolated as black microcrystals by crystallisation from THF : ethanol (1 : 1).

3.3. Reaction of C_{60} with excess $[Pt\{P(OPh)_3\}_4]$

To a solution of C_{60} (35 mg, 4.85×10^{-5} mol) in toluene (20 cm^3) $[Pt\{P(OPh)_3\}_4]$ was added first as a solution of (420 mg) in toluene (40 cm^3), and then as a solution of 140 mg in toluene (15 cm^3). The first addition caused development of a deep-green colour, but the second caused no further detectable colour change. The solution was slowly heated to 80°C, and finally refluxed (8 h). Solvent was removed under vacuum to a volume of ca. 20 cm^3, and this resulted in separation of unchanged $[Pt\{P(OPh)_3\}_4]$. The solution of the product was finally pumped to dryness, and the residue washed with methanol (4 × 20 cm^3). Subsequent work-up was as described under section 3.1. The product was analysed by HPLC, which gave two peaks attributable to compounds **(Ia)** and **(Ib)**, and these were isolated by preparative HPLC, (reverse phase C_{18} column eluted with toluene : acetonitrile (55 : 45).

Palladium analogues were obtained by procedures similar to those described in sections 3.2 and 3.3.

3.4. Mass spectrometry

Mass spectra were obtained with a VG ZAB-SE double-focusing instrument, (Fisons/V.G. Analytical, Manchester, UK) operating at 8 kV accelerating voltage, and a VG 11/250 J data system. An Ion Tech gun (Ion Tech Ltd., Teddington, UK) operating with Xe atoms at 8 kV was used to bombard samples loaded on a stainless-steel target previously smeared with 2 μL of 3-nitrobenzyl alcohol as matrix.

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