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Addition of the $[(^tBuP)_3As]^-$ anion to the cyclopentadienyl ring of $[(C_5H_5)M(CO)_3Cl]$ (M = Mo, W)

Alan Bashall,[a] Alexander D. Hopkins,[b] Martin J. Mays,*[b] Mary McPartlin,[a] Jody A. Wood,[b] Anthony D. Woods[b] and Dominic S. Wright*[b]

[a] *School of Chemistry, University of North London, London, UK N7 8DB*
[b] *Chemistry Department, University of Cambridge, Lensfield Road, Cambridge, UK.*
E-mail: dsw1000@cus.cam.ac.uk

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Reactions of the $[(^tBuP)_3As]^-$ anion with $[(C_5H_5)M(CO)_3Cl]$ (M = Mo, W) gives $[(C_5H_4\{As(P^tBu)_3\})M(CO)_3Cl]$ (M = Mo 1; M = W 2) as a result of addition to the C_5H_5 ring (with formal elimination of LiH), rather than the expected product resulting from substitution of the metal-bonded Cl ligand.

We recently showed that heterocyclic anions of the type $[(RP)_nE]^-$ (E = As, Sb; R = ^{t}Bu, cyclohexyl, 1-adamantyl) are accessible by the one-pot reactions of metallated aliphatic primary phosphines [RPHM; M = alkali metal] with $E(NMe_2)_3$ at low temperatures.[1] These anions have the potential to behave as sources of the Group 15 atoms (E) (*i.e.*, by elimination of $[RP]_n$), as is indicated by the formation of Zintl compounds containing E_7^{3-} anions in the reactions at higher temperatures.[1,2] A key step in the development of this area is the examination of the coordination characteristics and reactivity of the heterocyclic anions with a range of main group and transition metal complexes, with the ultimate aim of preparing molecular and extended phases by thermolysis. We report here the surprising finding that reaction of $[(^tBuP)_3As]^-$ with $[(C_5H_5)M(CO)_3Cl]$ (M= Mo, W) results in addition of the nucleophile to the cyclopentadienyl ring, rather than the anticipated exchange with the labile, metal-bonded Cl ligand.

The 1 : 1 reactions of the $[(^tBuP)_3As]^-$ anion (in the form of the Lewis base solvate $[(^tBuP)_3AsLi{\cdot}2DABCO{\cdot}thf]$[1b]) (DABCO = 1,4-diazabicyclo[2.2.2]octane) with $[(C_5H_5)M(CO)_3Cl]$ in toluene–thf were performed under argon. $[(C_5H_4\{As(P^tBu)_3\})Mo(CO)_3Cl]$ **1** and $[(C_5H_4\{As(P^tBu)_3\})W(CO)_3Cl]$ **2** were obtained as the isolable major products after aerobic workup, chromatography and crystallisation from hexane–CH_2Cl_2 (50 : 50).† An initial indication that addition of the $[(^tBuP)_3As]^-$ anion to the C_5H_5 rings of $[(C_5H_5)M(CO)_3Cl]$ had occurred[3] in **1** and **2** (with formal elimination of LiH) was provided by a combination of solution IR and ^1H spectroscopy. In particular, the room-temperature ^1H NMR spectra of both complexes exhibit two (1 : 1) cyclopentadienyl resonances (at δ 5.8 and 5.6 in **1** and 5.9 and 5.8 in **2**), while the solution IR spectra are almost identical with those of $[(C_5H_5)M(CO)_3Cl]$ in the CO region. The similarity of the room-temperature ^{31}P NMR spectra of **1** and **2** suggests that the $[(^tBuP)_3As]$ ring units in these complexes have similar chemical environments. Both are ABX systems, the inequivalence of the three P centres of the $[(^tBuP)_3As]$ ring units presumably resulting from restricted rotation about the C–As bonds of the $[C_5H_4\{As(^tBuP)_3\}]$ ligand.

Confirmation that the $[(^tBuP)_3As]$ unit is bonded to the C_5H_5 ring of $[(C_5H_5)Mo(CO)_3Cl]$ is provided by the X-ray structures of $[(C_5H_4\{As(P^tBu)_3\})Mo(CO)_3Cl]$ **1** and $[(C_5H_4\{As(P^tBu)_3\})W(CO)_3Cl]$ **2** (Fig. 1).‡ The metal–Cl [2.491(1) in **1** and 2.488(6) Å in **2**] bond lengths in both complexes are similar to those in $[(C_5H_5)M(CO)_3Cl]$ [M = Mo, 2.498(1); W, 2.490(2) Å],[4] as are the metal–CO distances [1.968(5)–2.021(6) in **1** and 2.01(2)–2.06(4) Å in **2**] compared to the unsubstituted precursors [range 1.980(4)–2.009(6) Å].[4] Substitution of a single cyclopentadienyl H by the sterically demanding $[(^tBuP)_3As]$ group does, however, cause some disruption in the bonding of the cyclopentadienyl ring to the metals. The M–C bonds in **1** and **2** are on average longer than those in $[(C_5H_5)M(CO)_3Cl]$, with the long C(11)–metal and C(15)–metal distances reflecting the position of the $[(^tBuP)_3As]$ substituent and the steric confrontation with the $M(CO)_3Cl$ fragments in both complexes. The tilting of the $[(^tBuP)_3As]$ rings in **1** and **2** [P(2) *ca.* 0.5 Å below the cyclopentadienyl ring plane and P(4) *ca.* 2.3 Å above] results in two spacially inequivalent terminal P centres (*exo* and *endo* to the metal), which are responsible for the ABX pattern in the ^{31}P NMR spectra. The geometries of the $[(^tBuP)_3As]$ rings of **1** and **2** most closely resemble those present in $[(^tBuP)_3As]_2$.[5] There are only small reductions in the ring P–As–P angles [82.62(5) in **1**, 82.9(1)° in **2**] and small increases in the P–As bond lengths [range 2.352(4)–2.362(1) Å in **1** and **2**] compared to those present in complexes containing $[(^tBuP)_3As]^-$ anions [*cf.* P–As–P *ca.* 85° and P–As 2.324(3)–2.336(1) Å[1,2]].

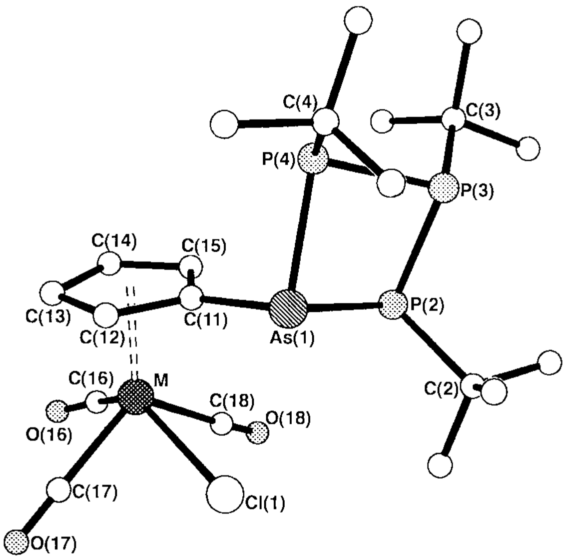

Fig. 1 Molecular structure of $[(C_5H_4\{As(P^tBu)_3\})M(CO)_3Cl]$ (M = Mo **1**, and M = W **2**). H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°); for **1**, Mo(1)–C(16) 1.968(5), Mo(1)–C(17) 2.003(6), Mo(1)–C(18) 2.021(6), Mo(1)–Cl(1) 2.491(1), Mo(1)–C(11) 2.378(4), Mo(1)–C(12) 2.318(5), Mo(1)–C(13) 2.285(5), Mo(1)–C(14) 2.300(5), Mo(1)–C(15) 2.359(5), As(1)–C(11) 1.973(4), As(1)–P(2) 2.360(1), As(1)–P(4) 2.362(1), P(2)–P(3) 2.228(2), P(3)–P(4) 2.220(2), P(2)–As(1)–P(4) 82.62(5), As(1)–P(2,4)–P(3) mean 87.60(5), P(2)–P(3)–P(4) 88.98(6); for **2**, W(1)–C(16) 2.06(4), W(1)–C(17) 2.01(2), W(1)–C(18) 2.05(2), W(1)–Cl(1) 2.488(6), W(1)–C(11) 2.37(1), W(1)–C(12) 2.31(1), W(1)–C(13) 2.31(1), W(1)–C(14) 2.32(1), W(1)–C(15) 2.36(1), As(1)–C(11) 1.96(1), As(1)–P(2) 2.352(4), As(1)–P(4) 2.359(4), P(2)–P(3) 2.230(5), P(3)–P(4) 2.218(4), P(2)–As(1)–P(4) 82.9(1), As(1)–P(2,4)–P(3) mean 87.5(1), P(2)–P(3)–P(4) 89.0(1).

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The fact that [$(C_5H_5)M(CO)_3Cl$] is uncharged and the expected low electrophilic character of the cyclopentadienyl C atoms, as well as the weakly nucleophilic nature of the [$(^tBuP)_3As$]$^-$ anion, make the observed addition of the nucleophile to the C_5H_5 ring in **1** and **2** (in preference to substitution of the potentially more reactive Cl ligands) particularly surprising.[6] Previous studies of an extensive range of cationic 18e transition metal complexes suggest that cyclopentadienyl ligands should have among the lowest reactivities towards nucleophiles compared to other π-bonded polyenes and that only strong nucleophiles (such as organometallic anions) will generally add to the ring.[7] It seems likely that the formation of **1** and **2** is primarily due to the large steric demands of the nucleophile, making bonding to the metal centres unfavourable and leading to thermodynamic rather than kinetic control of the reaction product. Steric factors have been invoked to explain unexpected selectivity in a few other nucleophilic addition reactions of this type involving sandwich complexes,[8] but not in half sandwich compounds like [$(C_5H_5)M(CO)_3Cl$] here.

The study of the reactions of [$(RP)_nE$]$^-$ anions with a more extensive range of organotransition metal compounds should be of great interest. The formation of **1** and **2** gives an initial indication that the reactivity patterns may not follow conventional wisdom. The simple and direct access to heteroatom-functionalised cyclopentadienyl derivatives described here may have considerable synthetic potential.

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Notes and references

† Synthesis of **1**; to a solution of [$\{(^tBuP)_3As\}Li\cdot 2DABCO\cdot thf$] (0.32 g, 0.5 mmol) in toluene (20 ml) and thf (2 ml) at −78 °C was added solid [$(C_5H_5)Mo(CO)_3Cl$] (0.14 g, 0.5 mmol). The mixture was stirred at this temperature (45 mins), giving a brown solution and then at *ca.* −10 °C (45 mins) before being allowed to reach room temperature. The solvent was removed under vacuum to give an orange-brown oil. Complex **1** was separated from unreacted [$(C_5H_5)Mo(CO)_3Cl$] (lower band) and [$(C_5H_5)Mo(CO)_3]_2$ (upper band) by thin layer chromatography on a silica plate (50:50 hexane–CH_2Cl_2), as the central orange band. Slow evaporation of this fraction from a hexane–CH_2Cl_2 (50:50) solution gave orange crystalline blocks of **1**. Yield of crystalline **1**, 0.054 g (20%). IR (solution in CH_2Cl_2), ν_{max} = 2052(s), 1974(s), 1927(w, sh). ^{1}H NMR (400 MHz, 25 °C, CD_3Cl), $\delta = 5.8$ (s, 2H, C–H C_5H_5) and 5.6 (s, 2H, C–H C_5H_5), 1.26 [d, (J_{P-H} = 13 Hz), 18H, terminal ^{t}BuP], 1.20 [d, (J_{P-H} = 12 Hz), 9H, central ^{t}Bu]. ^{31}P NMR (100.1 MHz, 25 °C, $CDCl_3$), $\delta = -39.6$ (d, $J = 131.7$ Hz), −39.6 (d, $J = 173.2$ Hz), −43.1 (dd, $J = 173.4$, 131.8 ± 0.1 Hz). Satisfactory elemental analysis (C, H) was obtained for **1**.

Complex **2** was prepared in an identical manner to **1**. It was separated as the central orange band from [$(C_5H_5)W(CO)_3Cl$] (lower band) and [$(C_5H_5)W(CO)_3]_2$ (upper band) by thin layer chromatography on a silca plate (50:50 hexane–CH_2Cl_2). Slow evaporation of this fraction from a hexane–CH_2Cl_2 (50:50) solution gave orange crystalline blocks of **2**. Yield of crystalline **2**, 0.011 g (3%, unoptimised). IR (solution in CH_2Cl_2), ν_{max} = 2044(s), 1957(s). ^{1}H NMR (400 MHz, 25 °C, CD_3Cl), $\delta = 5.9$ (s, 2H, C–H C_5H_5) and 5.8 (s, 2H, C–H C_5H_5), 1.25 [d, (J_{P-H} = 13 Hz), 18H, terminal ^{t}BuP], 1.21 [d, (J_{P-H} = 13 Hz), 9H, central ^{t}Bu]. ^{31}P NMR (100.1 MHz, 25 °C, $CDCl_3$), $\delta = -39.0$ (d), −39.0 (d), −43.4 (dd) (poorly resolved). Satisfactory elemental analysis (C, H) was obtained for **2**.

‡ Crystal data for **1**; $C_{20}H_{31}AsClMoO_3P_3$, $M = 618.67$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.308(2)$, $b = 16.303(4)$, $c = 10.132(2)$ Å, $\beta = 91.000(13)°$, $V = 2693.5(10)$ Å^3, μ(Mo–Kα) = 2.001 mm^{-1}, $T = 223(2)$ K. Data were collected on a Siemens P4 four circle diffractometer and corrected for absorption using ψ scans. Of a total of 7944 reflections collected, 3738 were independent ($R_{int} = 0.058$). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[9] Final $R1 = 0.030$ [$I > 2\sigma(I)$] and $wR2 = 0.064$ (all data).

Crystal data for **2**; $C_{20}H_{31}AsClWO_3P_3$, $M = 706.58$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 16.412(3)$, $b = 16.440(2)$, $c = 10.1301(16)$ Å, $\beta = 91.351(13)°$, $V = 2732.4(8)$ Å^3, μ(Mo–Kα) = 5.720 mm^{-1}, $T = 293(2)$ K. Data were collected on a Siemens P4 four circle diffractometer and corrected for absorption using ψ scans. Of a total of 6954 reflections collected, 3343 were independent ($R_{int} = 0.034$). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[9] Final $R1 = 0.069$ [$I > 2\sigma(I)$] and $wR2 = 0.175$ (all data). CCDC reference number 186/1971. See http://www.rsc.org/suppdata/dt/b0/b003687k/ for crystallographic files in .cif format.

1 (*a*) M. A. Beswick, N. Choi, A. D. Hopkins, M. E. G. Mosquera, M. McPartlin, P. R. Raithby, A. Rothenberger, D. Stalke, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1998, 2485; (*b*) A. Bashall, M. A. Beswick, N. Choi, A. D. Hopkins, S. J. Kidd, Y. G. Lawson, M. E. G. Mosquera, M. McPartlin, P. R. Raithby, A. E. H. Wheatley, J. A. Wood and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2000, 479.

2 See M. A. Beswick, J. M. Goodman, C. N. Harmer, A. D. Hopkins, M. A. Paver, P. R. Raithby, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1997, 1897; M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin and D. S. Wright, *Science*, 1998, **281**, 1500.

3 Although reaction ultimately occurs at the C_5H_5 rings the mechanism may involve initial addition of the nucleophile to the metal centres followed by transfer to the ligand, *e.g.*, W. Malisch, R. Malisch, I. J. Colquhoun and W. McFarlane, *J. Organomet. Chem.*, 1981, **220**, C1.

4 S. Chaiwasie and R. H. Fenn, *Acta Crystallogr., Sect. B*, 1968, **24**, 525; C. Bueno and M. R. Churchill, *Inorg. Chem.*, 1981, **20**, 2197.

5 M. Baudler, Y. Aktalay, T. Heinlein and K.-F. Tebbe, *Z. Naturforsch., Teil B*, 1982, **37**, 299.

6 For example, the reaction of Ph_2AsLi with [$(C_5H_5)_2TiCl_2$] results in substitution at the metal centre, S. R. Wade, M. G. H. Wallbridge and G. R. Willey, *J. Organomet. Chem.*, 1984, **267**, 271.

7 S. G. Davies, M. L. H. Green and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047.

8 For example, S. Rigney, J.-C. Leblanc, B. Nuber and C. Moise, *J. Chem. Soc., Dalton Trans.*, 1997, 1187 and references therein.

9 SHELXTL PC version 5.03, Siemens Analytical Instruments, Madison, WI, 1994.