Synthesis and Characterization of an Organoyttrium Dimer Produced via an Arbuzov Dealkylation Reaction

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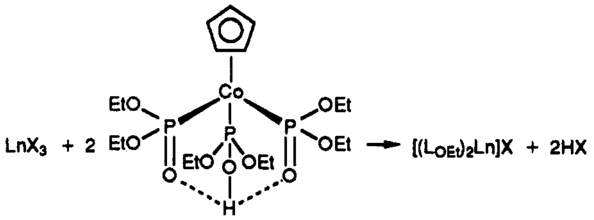
Summary: The reaction of anhydrous YCl_3 with 2 equiv of the sodium salt of the anionic tripod complex $[(\eta^5\text{-}C_5H_5)Co\{(CH_3CH_2O)_2P{=}O\}_3]^-$ (L_{OEt}) in tetrahydrofuran, under anaerobic conditions, leads to the high-yield formation of $[L_{OEt}Y\{(C_5H_5)Co(P({=}O)(OEt)_2)_2(P({=}O)(OEt)(O))\}_2YL_{OEt}]$ (1). The complex has been characterized by standard analytical techniques. Nuclear magnetic resonance spectroscopic studies show a reduction of local symmetry of one of the ligands. To clearly illustrate the structural features of the isolated complex in the solid state, a low-temperature data collection X-ray crystallographic investigation was performed. This study reveals 1 to be a dimer with bridging phosphonate oxygens (monoclinic system, space group $P2_1/n$, with a = 12.261 (4) Å, b = 21.110 (5) Å, c = 19.529 (5) Å, β = 94.77 (2)°, V = 5037 (6) Å^3, Z = 2, T = 102 (2) K, and D_{calcd} = 1.477 g/cm^3). The structure also shows that one of the phosphonate ethyl groups has been cleaved in the course of the reaction. Analysis of the volatiles generated during the reaction clearly shows the formation of ethyl chloride, indicating that 1 is produced in conjunction with the elimination of a phosphonate ethyl group in an Arbuzov-type dealkylation.

Introduction

Very little is known of the effects of an O-donor environment on the organometallic chemistry and homogeneous catalytic activity of transition-type complexes.[1] Feher[2] and Klemperer[3] have demonstrated that tridentate O ligands, trisilicates and $P_3O_9^{3-}$ can form stable organometallic complexes that can exhibit unusual chemical reactivity. Another such oxygen donor ligand is the anionic cobalt(III)-based oxygen tripod $[(\eta^5\text{-}C_5H_5)Co\{(CH_3CH_2O)_2P{=}O\}_3]^-$ (L_{OEt}), developed by Klaui and coworkers.[4] This ligand is in many respects similar to the cyclopentadienyl (Cp) ligand and its derivatives, which have proven of great use in organometallic chemistry. The L_{OEt} anion has also been postulated as more oxidatively robust[5] than the Cp ligand and as a prototype for transition-metal–surface model studies.[4c,6]

With few notable exceptions,[7-9] the ancillary ligation appended to early transition and lanthanoid metals has revolved around nitrogen- and oxygen-based donors.[10] This is easily understood in view of the well-known "hard", oxophilic nature of these metal centers.[11] Klaui has reported the synthesis and isolation of cationic lanthanide complexes from the reaction of lanthanide halides with $H[(\eta^5\text{-}C_5H_5)Co\{(CH_3CH_2O)_2P{=}O\}_3]$ in an aqueous medium[12] according to eq 1. Considering the noted preference for oxygen-based ligands of the lanthanide and pseudo-lanthanide metal centers, as reflected by the magnitude of organolanthanide–oxygen bond dissociation enthalpies,[13] it is surprising to notice that reactions between lanthanide chlorides and 2 equiv of NaL_{OEt} had not been examined. Our interest in alternative lanthanide and early-transition-metal ancillary ligation prompted us to examine the reactivity of lanthanide and pseudo-lanthanides toward this O-donor ligand. We report in the present contribution the synthesis as well as the spectral and structural characterization of a L_{OEt}-based yttrium complex. A plausible reaction pathway involved in the present system is also discussed.



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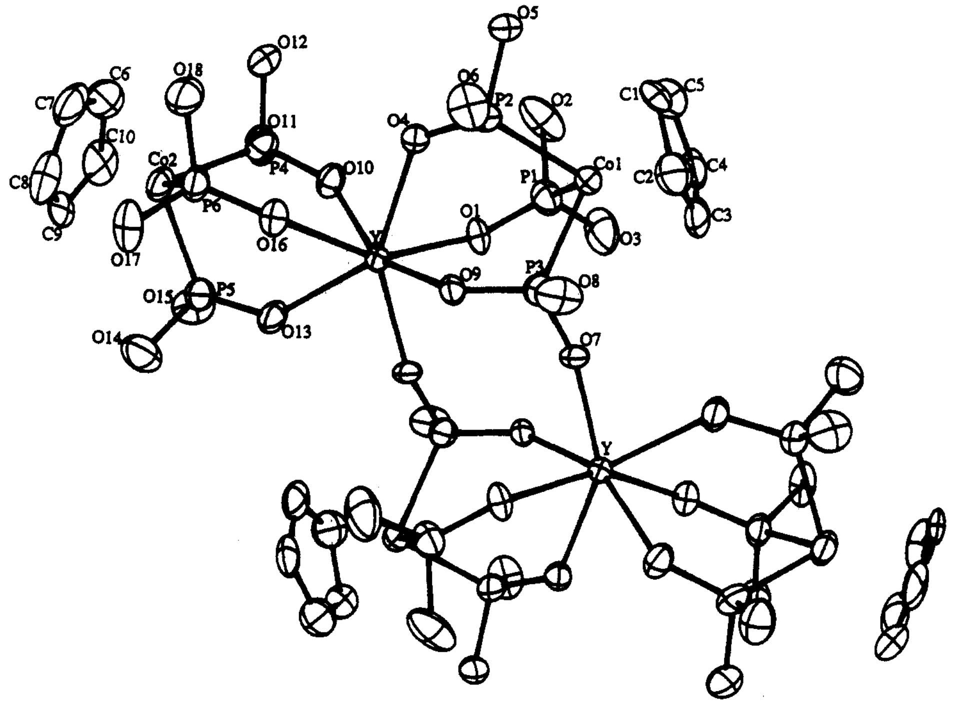

Figure 1. Molecular structure of $[L_{OEt}Y\{(C_5H_5)Co(P({=}O)(OEt)_2)_2(P({=}O)(OEt)(O))\}_2YL_{OEt}]$ (1) with probability ellipsoids drawn at the 50% level. Ethyl groups have been omitted to clarify the structure.

Experimental Section

General Considerations. All reactions and manipulations were carried out under an argon or nitrogen atmosphere using standard Schlenk-line and high-vacuum-line techniques or in a Vacuum Atmospheres glovebox. Solvents used were predried over Na wire and freshly distilled from Na/K alloy. Yttrium chloride (99.9%) was purchased from Cerac Chemicals and used as received. The sodium salt of the anionic ocmplex L_{OEt} was synthesized according to published procedures.[4] Nuclear magnetic resonance spectra (^{1}H, ^{13}C, ^{31}P) were recorded on a Varian 400-MHz Unity spectrometer and are referenced to TMS and H_3PO_4. Infrared spectra were recorded on Nujol mulls sandwiched between KBr plates by use of a Perkin-Elmer Model 1760 spectrophotometer. Elemental analysis was performed at Oneida Research Services, Whitesboro, NY.

Synthesis of $[L_{OEt}Y\{(C_5H_5)Co(P({=}O)(OEt)_2)_2(P({=}O)(OEt)(O))\}_2YL_{OEt}]$ (1). In the glovebox, 2.86 g (5.12 mmol) of NaL_{OEt} and 0.50 g (2.56 mmol) of anhydrous YCl_3 were charged into a 25-mL flask of a vacuum-line frit assembly. The frit assembly was removed from the glovebox and attached to the high-vacuum line, where 15 mL of THF was vacuum-transferred onto the solids. The reaction mixture was warmed to room temperature while being stirred and then heated to 69 °C for 12 h. After this time, the yellow solution containing a white suspension was cooled to room temperature. The volatiles were then removed in vacuo, and 20 mL of toluene was used to extract 1. The volume of the solution was reduced by half, and the remaining clear yellow solution was slow-cooled to −78 °C. Crystallization in this manner, followed by cold filtration, afforded yellow microcrystals of 1 (1.26 g, 1.28 mmol, 87% yield). Anal. Calcd for $C_{64}H_{130}O_{36}P_{12}Co_4Y_2$: C, 34.0; H, 5.8. Found: C, 34.3; H, 5.8. IR (KBr): 2956 (vs), 2880 (vs), 1459 (m), 1123 (s), 1047 (m), 1026 (m, sh), 995 (w), 832 (w), 735 (m), 586.3 (m) cm^{-1}. ^{1}H NMR (C_7D_8): δ 5.36 (s, C_5H_5, 5 H), 5.03 (s, C_5H_5, 5 H), 4.0–5.0 (m, OCH_2CH_3, 22 H), 1.2–1.6 (m, OCH_2CH_3, 33 H). ^{13}C NMR (C_7H_8): δ 89.78 (s, C_5H_5), 89.53 (s, C_5H_5), 58–62 (m, OCH_2CH_3), 16–18 (m, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (C_7H_8): δ 20.5 (t, $\Delta\nu_{1/2} = 13$ Hz, $^2J_{PP} = 146$ Hz), 17.8 (t, $\Delta\nu_{1/2} = 13$ Hz, $^2J_{PP} = 146$ Hz), 11.4 (s, $\Delta\nu_{1/2} = 40$ Hz), −33.3 (t, $\Delta\nu_{1/2} = 13$ Hz, $^2J_{PP} = 142$ Hz).

Crystallographic Study. A yellow crystal grown by slow cooling of a toluene solution of 1 (approximate dimensions 0.15 × 0.25 × 0.50 mm, needle-shaped crystal) was mounted on an Enraf-Nonius CAD 4 diffractometer, and data were collected at 102 K. The structure was solved using direct methods and refined by full-matrix least-squares techniques. The crystal data and data collection parameters are summarized in Table I. Selected bond distances and angles are presented in Table II. Positional and equivalent isotropic thermal parameters are presented in Table III.

Table I. Summary of Crystallographic Data for 1

empirical formula	$(YCo_2P_6O_{18}C_{32}H_{65})_2$
space group	$P2_1/n$
unit cell dimens	
a, Å	12.261 (4)
b, Å	21.110 (5)
c, Å	19.529 (5)
α, deg	90
β, deg	94.77 (2)
γ, deg	90
V, Å^3	5037 (6)
Z, molecule/cell	2
density (calcd), g/cm^3	1.477
wavelength, Å	0.71073
monochromator	highly ordered graphite cryst
temp, K	102 (2)
abs cor	empirical (4-scan method)
diffractometer	Enraf-Nonius CAD 4
scan type	θ–2θ
data collected	$+h,+k,\pm l$
2θ range, deg	2.0–44.0
no. of collected rflns	5576
no. of indep rflns	5322
no. of obsd rflns	3323
R_I, %	2.4
R_F (obsd data), %	6.5
R_{WF}, %	8.8
goodness of fit	2.89
no. of variables	532

Results and Discussion

Reaction of anhydrous YCl_3 with 2 equiv of NaL_{OEt} in refluxing tetrahydrofuran followed by extraction with toluene or diethyl ether leads to the isolation of a yellow crystalline material in high yield. ^{1}H and ^{13}C NMR spectroscopic results indicate the presence of two inequivalent Cp rings in the isolated complex, not consistent with a complex having $(L_{OEt})_2Ln{-}Cl$ stoichiometry. This $(L_{OEt})_2Ln{-}Cl$ stoichiometry was expected in view of recent work by Baudry and co-workers,[14] who reported the syn-

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for 1

Bond Lengths			
Y···Y	5.645 (2)	Y···Co(1)	4.243 (2)
Y···Co(2)	4.339 (2)	Y–O(1)	2.254 (6)
Y–O(4)	2.407 (6)	Y–O(7)	2.242 (5)
Y–O(9)	2.252 (6)	Y–O(10)	2.279 (6)
Y–O(13)	2.445 (7)	Y–O(16)	2.305 (6)
Co(1)–P(1)	2.159 (3)	Co(1)–P(2)	2.164 (3)
Co(1)–P(3)	2.206 (3)	Co(2)–P(4)	2.160 (3)
Co(2)–P(5)	2.160 (3)	Co(2)–P(6)	2.166 (3)
P(3)–O(9)	1.527 (7)	P(3)–O(7)	1.500 (7)
P(3)–O(8)	1.623 (7)	P(1)–O(1)	1.502 (6)
P(2)–O(4)	1.504 (6)	Co(1)–Cp^1	1.710 (3)
		Co(2)–Cp^2	1.716 (3)
Bond Angles			
Y–O(1)–P(1)	135.1 (4)	Y–O(4)–P(2)	129.8 (3)
Y–O(7)–P(3)	163.3 (5)	Y–O(9)–P(3)	131.9 (4)
Y–O(10)–P(4)	139.3 (4)	Y–O(13)–P(5)	136.5 (4)
Y–O(16)–P(6)	137.9 (4)	O(1)–Y–O(4)	76.6 (2)
O(1)–Y–O(7)	81.3 (2)	O(1)–Y–O(9)	84.9 (2)
O(1)–Y–O(13)	126.1 (2)	O(1)–Y–O(16)	150.7 (2)
O(4)–Y–O(9)	74.8 (3)	O(1)–Y–O(10)	79.2 (2)
P(1)–Co(1)–Cp	124.1 (3)	P(2)–Co(1)–Cp	125.4 (3)
P(3)–Co(1)–Cp	124.1 (3)	P(4)–Co(2)–Cp	123.8 (3)
P(5)–Co(2)–Cp	124.8 (3)	P(6)–Co(2)–Cp	124.6 (3)

Scheme I

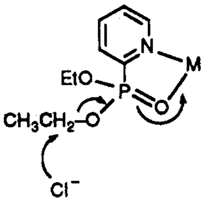

Table III. Positional and Equivalent Isotropic Thermal Parameters for 1[a]

atom	x	y	z	B,[b] Å^2
Y	0.9913 (1)	−0.08719 (6)	1.10834	1.75 (3)
Co(1)	0.9575 (2)	0.10666 (9)	1.15448 (9)	2.34 (5)
Co(2)	0.9923 (2)	−0.27321 (9)	1.2002 (1)	2.74 (5)
P(1)	1.1107 (4)	0.0567 (2)	1.1565 (2)	3.1 (1)
P(2)	0.8907 (4)	0.0323 (2)	1.2138 (2)	3.0 (1)
P(3)	1.1059 (4)	−0.0603 (2)	0.9419 (2)	2.4 (1)
P(4)	1.0958 (4)	−0.1955 (2)	1.2356 (2)	2.7 (1)
P(5)	1.0338 (4)	−0.2578 (2)	1.0964 (2)	2.9 (1)
P(6)	0.8499 (4)	−0.2135 (2)	1.1820 (2)	2.6 (1)
O(1)	1.1138 (8)	−0.0088 (4)	1.1277 (5)	2.2 (2)
O(2)	1.1623 (9)	0.0561 (5)	1.2364 (6)	4.8 (3)
O(3)	1.2060 (1)	0.0964 (5)	1.1259 (6)	5.2 (3)
O(4)	0.9309 (8)	−0.0341 (4)	1.2068 (4)	2.3 (1)
O(5)	0.9136 (9)	0.0546 (5)	1.2924 (4)	3.3 (3)
O(6)	0.7582 (8)	0.0328 (5)	1.2097 (5)	3.3 (3)
O(7)	1.0467 (8)	−0.794 (4)	1.0025 (4)	2.6 (2)
O(8)	1.2295 (8)	−0.871 (5)	0.9559 (5)	3.5 (3)
O(9)	0.8784 (8)	−0.0107 (4)	1.0653 (4)	2.2 (2)
O(10)	1.0953 (8)	−0.1362 (4)	1.1948 (5)	2.7 (2)
O(11)	1.2183 (9)	−0.2173 (5)	1.2503 (5)	3.7 (3)
O(12)	1.068 (1)	−0.1794 (5)	1.3120 (5)	4.1 (3)
O(13)	1.0295 (9)	−0.1930 (4)	1.0674 (5)	3.4 (3)
O(14)	0.967 (1)	−0.3043 (5)	1.0430 (5)	4.7 (3)
O(15)	1.1511 (8)	−0.2883 (5)	1.0932 (5)	3.7 (3)
O(16)	0.8572 (8)	−0.1517 (4)	1.1449 (4)	2.5 (2)
O(17)	0.7557 (8)	−0.2559 (5)	1.1432 (5)	3.3 (3)
O(18)	0.7920 (9)	−0.2022 (5)	1.2520 (5)	4.4 (3)
C(1)	0.887 (2)	0.1748 (7)	1.2140 (7)	4.3 (4)
C(2)	0.852 (2)	0.1840 (8)	1.1420 (8)	4.1 (4)
C(3)	0.953 (1)	0.1955 (7)	1.1098 (8)	4.0 (4)
C(4)	1.039 (1)	0.1936 (7)	1.1610 (8)	3.3 (4)
C(5)	1.001 (1)	0.1798 (8)	1.2232 (8)	3.9 (4)
C(6)	1.037 (2)	−0.3234 (8)	1.2905 (8)	5.6 (5)
C(7)	0.923 (2)	−0.3288 (8)	1.2739 (9)	5.4 (5)
C(8)	0.907 (1)	−0.3567 (7)	1.2094 (9)	4.2 (5)
C(9)	1.1009 (2)	−0.3700 (6)	1.1892 (8)	4.0 (4)
C(10)	1.089 (1)	−0.3470 (7)	1.2377 (9)	4.2 (4)
C(11)	1.240 (2)	0.0133 (9)	1.2608 (8)	5.8 (5)
C(12)	1.256 (2)	0.021 (1)	1.336 (1)	8.4 (7)
C(13)	1.225 (2)	0.0990 (9)	1.0591 (9)	9.6 (7)
C(14)	1.321 (2)	0.129 (1)	1.036 (1)	10.2 (8)
C(15)	0.885 (2)	0.0145 (8)	1.3461 (8)	5.1 (5)
C(16)	0.922 (2)	0.042 (1)	1.4150 (9)	10.4 (8)
C(17)	0.689 (1)	−0.0095 (7)	1.1663 (8)	3.8 (4)
C(18)	0.575 (2)	−0.003 (1)	1.183 (1)	7.7 (7)
C(19)	1.286 (2)	−0.084 (1)	1.019 (1)	9.1 (7)
C(20)	1.391 (2)	−0.112 (1)	1.022 (1)	7.4 (7)
C(23)	1.299 (2)	−0.2054 (9)	1.206 (1)	5.9 (5)
C(24)	1.380 (2)	−0.160 (1)	1.233 (1)	6.6 (6)
C(25)	1.103 (2)	−0.1209 (9)	1.3424 (8)	4.7 (5)
C(26)	1.078 (2)	−0.120 (1)	1.4156 (9)	6.8 (6)
C(27)	0.876 (2)	−0.289 (1)	1.000 (1)	7.3 (6)
C(28)	0.870 (2)	−0.327 (1)	0.934 (1)	7.5 (6)
C(29)	1.206 (2)	−0.285 (1)	1.0327 (9)	6.1 (5)
C(30)	1.293 (2)	−0.331 (1)	1.036 (1)	8.7 (8)
C(31)	0.649 (2)	0.2277 (9)	1.131 (1)	6.6 (6)
C(32)	0.577 (2)	−0.267 (1)	1.085 (1)	7.5 (7)
C(33)	0.798 (2)	−0.1491 (8)	1.2911 (9)	6.2 (5)
C(34)	0.728 (3)	−0.148 (1)	1.340 (1)	18.3 (8)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

thesis of organouranium complexes supporting the L_{OEt} ligation using the synthetic metathetical pathway illustrated in eq 2. The $^{31}P\{^1H\}$ NMR spectrum of the isolated

$$\mathrm{UCl_4 + 2NaL_{OEt} \rightarrow (L_{OEt})_2UCl_2 + 2NaCl} \qquad (2)$$

yttrium complex exhibits four inequivalent phosphorus resonances, three of which show phosphorus–phosphorus coupling.[15] The complex appears to have a static structure, for no fluxonial behavior was observed by NMR at temperatures ranging from −80 to +80 °C.

In order to unequivocally determine the structure of the isolated crystalline material, an X-ray single-crystal diffraction study was performed at low temperature. The results of this study clearly show the molecule to consist of a dimeric arrangement of seven-coordinate yttrium centers (Figure 1). The structure is symmetrical about an inversion center and reveals the absence of Cl atoms as well as the cleavage of a phosphonate ethyl group, making possible the dimeric linkage. The informative bond distances are the Y–O(7) and Y–O(9) values of 2.242 (5) and 2.252 (6) Å, respectively, which reflect similar bond distances between yttrium centers and the bridging and nonbridging phosphonate oxygens of the bridging L_{OEt} ligand. The phosphorus–oxygen distances also point out the different atom connectivity in the bridging arrangement; specifically, the P(3)–O(7) and P(3)–O(9) distances, representing bonds in the Y–O–P linkage, are similar at 1.500 (7) and 1.527 (7) Å, respectively. The remaining P(3)–O(8) distance in the bridging phosphonate fragment, part of the POEt linkage, has a longer bond distance, 1.623 (7) Å.

A possible pathway followed in the present reaction can be postulated by examining results reported on the related (diethyl 2-pyridylphosphonato)ruthenium system, recently investigated by Huang and co-workers.[16] These researchers observed direct attack on the phosphonate ligand

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(14) Baudry, D.; Ephritikhine, M.; Kläui, W.; Lance, M.; Nierlich, M.; Vigner, J. *Inorg. Chem.* **1991**, *30*, 2333–2336.

(15) For examples of $^2J_{PP}$ coupling see: Finer, E. G.; Harris, R. K. Spin-Spin Coupling Between Phosphorus Nuclei. In *Progress in NMR Spectroscopy*; Emsley, J. W., Feeney, J.; Sutcliffe, L. H., Eds.; Pergamon Press: New York, 1970; Chapter 2.

(16) Huang, Y.-S.; Chaudret, B.; Bellan, J.; Mazieres, M.-R. *Polyhedron* **1991**, *10*, 2229–2233.

by chloride ions in an Arbuzov-type dealkylation[17] leading to the formation of phosphonate-bridged dimers. Such a mechanism has also been reported to occur during the formation of $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(CO)(NR_2)_n(OR')_{2-n}\}]$ (n = 1, 2).[18] The identification of ethyl chloride by GC-MS[19] as a volatile material generated in the course of the reaction, along with the structural characterization of 1, leads us to believe that the reaction mechanism involved in the present system is similar to those mentioned above. On the basis of experimental spectroscopic and crystallographic results, the overall reaction stoichiometry is proposed to proceed as illustrated in eq 3.

$$2YCl_3 + 4NaL_{OEt} \rightarrow [L_{OEt}Y\{(C_5H_5)Co(P(=O)(OEt)_2)_2(P(=O)(OEt)(O))\}_2YL_{OEt}] + 4NaCl + 2EtCl \quad (3)$$

1

Concluding Remarks

A straightforward synthetic route is used in the isolation of the unusual dimeric complex 1 containing a L_{OEt} ligand in a normal tripod chelating mode as well as in an unusual bridging fashion, accessible via phosphonate ethyl loss. To our knowledge, this is the first example of an Arbuzov-type dealkylation reaction involving an yttrium complex. Our current efforts are directed toward gauging the scope of this reaction type in lanthanide chemistry as well as investigating the reactivity of the present yttrium dimer.

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Supplementary Material Available: Tables of crystal intensity data, selected distances and angles, and anisotropic thermal parameters for 1 (15 pages). Ordering information is given on any current masthead page.

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[17] For a review of the Arbuzov reaction see: Arbuzov, B. A. *Pure Appl. Chem.* 1964, *9*, 307-335.

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[19] Mass spectrometry results for EtCl (70 eV): *m/e* 64 ($Et^{35}Cl$), 66 ($Et^{37}Cl$), in the correct isotopic ratio.

Regiospecific Mono-Transmetalation of 4-Stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacenes

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Summary: The reactivity of $BrMn(CO)_5$ toward two 4-stannatetrahydro-*s*-indacenes 1 and 7 is described. Only mono-transmetallation products were obtained. Regiospecific mono-transmetallation is found when compound 7 and $BrMn(CO)_5$ are reacted.

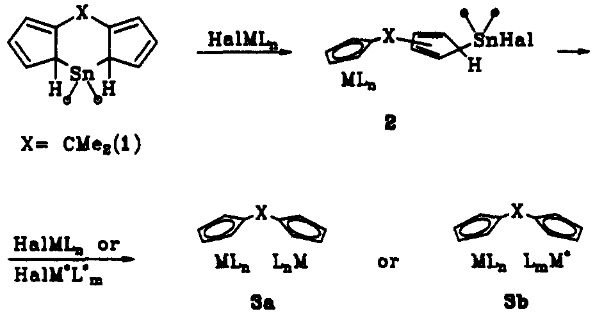
η^1-Cyclopentadienyl derivatives of group 4A elements are known to undergo a smooth substitution reaction with transition-metal halides to yield both sandwich and half-sandwich η^5 complexes. This reaction has been employed widely as a convenient method to obtain several η^5-Cp derivatives:[1,2]

(1)

El= Si, Ge, Sn

Recently we published the protocol for the synthesis of 4-stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene (1).[3] Compound 1 and its analogs can be successfully used for the synthesis of mono- and binuclear η^5-Cp derivatives of the types 2 and 3, which are currently the focus of interest (Scheme I).[4]

Scheme I



For the preparation of heterometallic compounds the synthetic procedure will be efficient only if the reactivity of a given $HalML_n$ species toward 1 or its analogs (X = CMe_2) is significantly higher than that toward 2. Given this condition, it is possible to isolate from the reaction mixture of 1 with $HalML_n$ the main product 2 in high yield and, subsequently, to introduce 2 in the reaction with any other active transition-metal halide complex to yield the heterometallic compound 3b. If this is not the case, generally a mixture of 2 and 3a would be the result.

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