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Coordination chemistry of perhalogenated cyclopentadienes and alkynes—XX.† Synthesis of bi- and trimetallic cymantrene derivatives with silver or gold containing ring substituents. First observation of oxidative addition of a halogen-cyclopentadienyl bond to a Ni^0 fragment

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Abstract—Treatment of the perhalogenated cymantrenes $[C_5X_4Br]Mn(CO)_3$ (X = Cl, Br) with butyl lithium and $Au(PPh_3)Cl$ yields, depending on the reaction conditions, the bi- or trimetallic σ, π-bridged cyclopentadienyl complexes $[C_5X_{5-n}(AuPPh_3)_n]Mn(CO)_3$ with $n = 1$ or 2. Similarly, the bimetallic complexes $[C_5Cl_4(AgPPh_3)]Mn(CO)_3$ and $[C_5Cl_4(AuCN^tBu)]Mn(CO)_3$ can be obtained. Addition of $Ni[PBu_3]_2(C_2H_4)$ to $[C_5Cl_4(AuPBu_3)]Mn(CO)_3$ generated *in situ* results in oxidative addition of one ring CCl bond to Ni^0 to give $[C_5Cl_3(AuPBu_3)[Ni(PBu_3)_2Cl]]Mn(CO)_3$, the first complex with three different metals attached to one cyclopentadienyl ring. When the lithium cymantrenyl thiolates $[C_5Cl_3X(SLi)]Mn(CO)_3$ (X = Cl, Li or SLi) are treated with $Au(PPh_3)Cl$, the gold thiolates $[C_5Cl_3Y(SAuPPh_3)]Mn(CO)_3$ with Y = Cl, $AuPPh_3$ or $SAuPPh_3$ are formed. © 1997 Elsevier Science Ltd

Keywords: cymantrene; oxidative addition; gold complexes; silver complexes; nickel complexes; cyclopentadienyl thiolate ligands.

The examination of hydrocarbon bridged bi- and polymetallic complexes is a subject of continuous interest [2]. One important subgroup of these compounds are metallocenes containing cyclopentadienyl rings as σ,π-bridges between two metal fragments [3]. The usual synthetic strategy involves deprotonation of the π-coordinated cyclopentadienyl ligand with consecutive addition of a transition metal halide complex. However, by this route, only bimetallic complexes could be obtained so far. A very unusual double C—H-activation in $CpRe(CO)_3$ by Cp_2ZrN^tBu to give a trimetallic bis-zirconyl species was discovered only recently by Bergman *et al.* [4]. Only electrophilic mercuration with $Hg(OOCCR_3)_2$ has been reported to introduce one, two or five Hg-substituents into the cyclopentadienyl ring [5].

Bromine–lithium exchange in $[C_5Cl_4Br]Mn(CO)_3$, followed by addition of halide complexes L_nM—X affords bimetallic complexes $[C_5Cl_4ML_n]Mn(CO)_3$ with $ML_n = Mn(CO)_5$ [6], $Au(PPh_3)$ [6], Cp_2TiCl [7], Cp_2HfCl [7], $[Cp_2Ti]_{0.5}$ [7]. However, in contrast to similar mononuclear tetrachlorocymantrene derivatives with donor substituents like SMe [8], further addition of butyllithium resulted only in exchange of the metal fragment for lithium and thus, polynuclear derivatives were not accessible by this route either. Recent mechanistic studies on $[C_5X_4Br]Mn(CO)_3$ (X = Cl, Br) showed the possibility of introducing two lithium atoms simultaneously into the ring to give a species that may be formulated as

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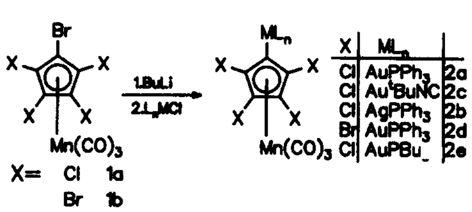
† For Part XIX, see [1].

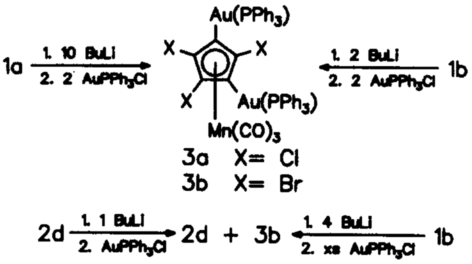
"$[C_5X_3Li_2]Mn(CO)_3$" [9]. Here we report about studies towards the synthesis of trimetallic cymantrene derivatives, where two gold containing complex fragments are either bound directly or *via* a thiolate-"link" to the cyclopentadienyl ring.

RESULTS AND DISCUSSION

Treatment of $[C_5Cl_4Br]Mn(CO)_3$ (**1a**) with butyl lithium and $Au(PPh_3)Cl$ yields $[C_5Cl_4(AuPPh_3)]Mn(CO)_3$ (**2a**) [6]. Similarly, addition of $Ag(PPh_3)_3Cl$ or $Au(t\text{BuNC})Cl$ gives the corresponding complexes **2b** and **2c**, respectively. The analogous reaction of $[C_5Br_5]Mn(CO)_3$ (**1b**) with BuLi and $Au(PPh_3)Cl$ gives $[C_5Br_4(AuPPh_3)]Mn(CO)_3$ (**2d**) (eq. (1)).



(Eq. 1)



(Eq. 2)

While Ag [10] and Au [6,11] containing ring substituted derivatives are known for several metallocenes, neither silver phospine nor gold isocyanide derivatives have been reported so far.

When **1a** is treated with ten equivalents of butyl lithium in THF, the intermediate "$[C_5Cl_3Li_2]Mn(CO)_3$" can be isolated by precipitation with hexane at $-78°C$ [9]. Addition of $Au(PPh_3)Cl$ to a THF solution of this compound yields the trimetallic complex $[C_5Cl_3(AuPPh_3)_2]Mn(CO)_3$ (**3a**). Consecutive treatment of $[C_5Br_5]Mn(CO)_3$ (**1b**) with two equivalents of butyl lithium and $Au(PPh_3)Cl$ each gives the corresponding tribromocymantrenyl derivative **3b**.

Although **2b** is stable in the solid state in a freezer, CH_2Cl_2 solutions decompose at r.t. within 60 min with quantitative formation of $[C_5Cl_4H]Mn(CO)_3$, which is always contaminating **2b**. Therefore it was not possible to obtain satisfactory elemental analyses for this compound. All the gold-containing compounds reported here are much more stable and usually allowed full characterization. IR and NMR spectroscopic data are summarized in Table 1.

Two features of these data merit a short discussion. First, introducing one Ag- or Au-fragment into the perhalocyclopentadienyl ring results in a bathochromic shift of the $\nu(CO)$ (A_1)-band by *ca* 20 cm^{-1} in comparison to the starting compounds. When two metal fragments are σ-bonded to the cyclopentadienyl ring, another bathochromic shift of 20–25 cm^{-1} results. Parallel to this, the CO peaks in the ^{13}C-NMR spectrum shift by approximately 4 ppm to lower field for each metal fragment introduced. This means a relatively drastic increase of electron density at the manganese center, when additional metals become σ-coordinated to the cyclopentadienyl ring. The second interesting observation concerns the ^{13}C-NMR signals of the cyclopentadienyl ring carbons. The *ipso*-carbon atoms which can easily be identified by their large couplings to the ^{31}P nuclei become drastically shifted to lower field when going from the dinuclear complexes **2** to the trinuclear complexes **3**. ^{13}C-NMR signals for cyclopentadienyl carbons are usually only observed in this region of the spectrum, when the ring is coordinated to a highly Lewis acidic center such as Ti^{IV}.

Treatment of **2d** with butyl lithium and $Au(PPh_3)Cl$ yields a mixture of **2d** and **3b**. Also, when **1b** is treated with four equivalents of butyl lithium and $Au(PPh_3)Cl$, the only phosphorus-containing species (^{31}P-NMR identification) are **2d** and **3b** besides unreacted $Au(PPh_3)Cl$. (eq. 2)).

These results show the difference between perhalogenated cyclopentadienyl complexes and their unsubstituted counterparts: while in complexes **1** auration occurs at two *different* carbon atoms, in the latter compounds either exclusive monosubstitution is observed, or the second "$Au(PR_3)$" fragment attacks the *ipso* carbon, giving 1,1 diaurated species with Au—Au bonds [12]. However, a further σ-metalation seems not to be possible *via* the route outlined so far. This shows the strong influence of the incoming electrophile, since introduction of up to five H [9] —SR [8] or —SiR_3 [13] functionalities is possible, as mentioned above.

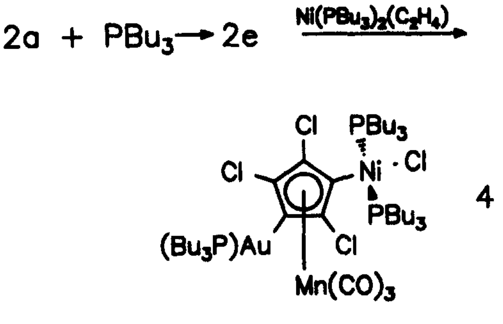
Nevertheless, we turned to another approach to the synthesis of poly-σ-metallated cyclopentadienyl complexes. Besides the common oxidative addition of uncomplexed haloarenes, π-complexed haloarenes have also been reported to undergo this reaction with Pd^0 compounds [14]. We wondered if an oxidative addition reaction of a d^{10} metal fragment across a carbon halogen bond of a halogenated cyclopentadienyl complex would work. From several screening experiments we learned that the reduction mixture from $Ni(PBu_3)_2Cl_2$ and sodium dust under ethylene was a good "candidate" for performing such a reaction with a perhalogenated cymantrene. We chose **2a** as a starting compound with one fragment already σ-coordinated, but met problems due to phosphine exchange reactions with the nickel reduction mixture.

Table 1. IR and NMR spectroscopic data[a]

Compound	IR : ν(CO) [cm^{-1}]	^{31}P-NMR	$\delta(^{13}CO)$	$\delta(^{13}C_5R_5)$,($J_{C\text{-}P}$, Hz)
2a	2024s, 1952vs, 1934s	42.3		110.6d [119], 103.6s, 99.1d [6]
2b	2021s, 1932s[b]	6.8[c]	—	—
2c	2031s, 1946s	—	—	—
2d	2018s, 1947s, 1930s	41.4	225.1	120.5d [120], 93.5s, 90.9d [6]
2e	2025s, 1940s	20.2	224.5	112.1s, 104.0s, 98.9s
3a	2004s, 1923vs	42.2	228.0	117.8dd [119; 2], 107.7d [8], 105.7d [11][d]
3b	2006s, 1925vs[c]	41.2	228.3	126.0d [120], 102.2s, 96.7d [8][d]
4	2004s, 1918s	30.2s, 2.3d, 0.2d[e]	227.5	—
6a	2028s, 1973s, 1947s	37.0[c]	222.1	103.9s, 96.1s, 95.7s
6b	2012vs, 1953s, 1920s	42.3s, 36.2br, s[c]	—	—
6c	2013s, 1934s	34.3br[c]	225.2	106.0s, 100.3s, 98.4s

[a] IR spectra of Nujol mulls except where indicated. NMR spectra in C_6D_6 except where indicated.
[b] In Et_2O.
[c] In CH_2Cl_2.
[d] AXX′ or AX_2 spin systems.
[e] AB system, $J_{AB} \approx 322$ Hz.

Substitution of the PPh_3 ligand with PBu_3 should overcome this problem, which was easily performed by addition of PBu_3 to **2a** to give $[C_5Cl_4(AuPBu_3)]Mn(CO)_3$ (**2e**). When solutions of this compound and of $Ni(PBu_3)_2(C_2H_4)$ are mixed, the desired oxidative addition reaction of a metallocene cyclopentadienyl-halogen bond to the d^{10} metal fragment actually takes place and the trimetallic complex $[C_5Cl_3(AuPBu_3)(Ni(PBu_3)_2Cl)]Mn(CO)_3$ (**4**) is obtained (eq. (3)). This constitutes not only a new reaction type of cyclopentadienyl complexes, but also the first synthesis of a cyclopentadienyl complex with three different metals attached to the same ring.



(Eq. 3)

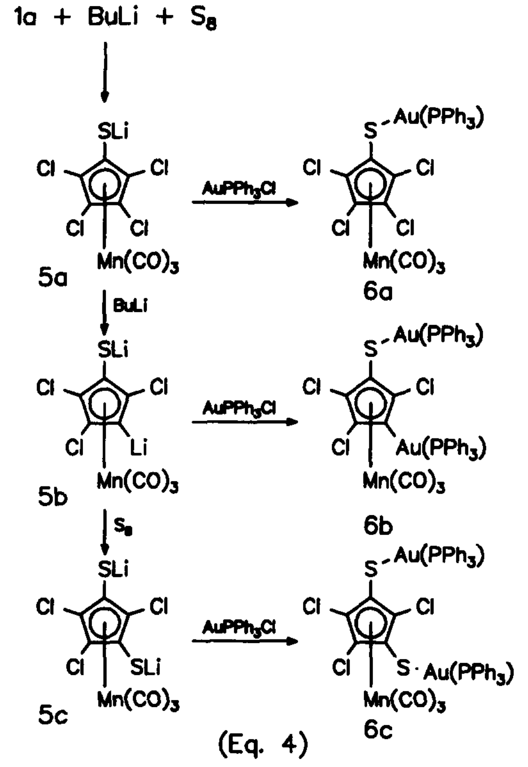
Thiolate complexes

Gold thiolates have been an object of widespread interest for a long time [15]. Besides studies directed towards possible applications of these compounds, several groups were interested mainly in structural aspects. This was mainly driven by the search for further representatives of compounds with Au—Au bonds. Thus, spectroscopic studies [16] as well as crystal structure determinations of gold phosphine derivatives of aromatic mono- or bis-thiolates, even of benzene hexathiolate, have been performed [17]. But also derivatives with perhalophenylmercaptides [18] and with ferrocene residues [19] have been studied.

Several years ago we reported that treatment of **1a** with butyl lithium and elemental sulfur results in precipitation of $[C_5Cl_4(SLi)]Mn(CO)_3$ (**5a**) [20]. This product can be redissolved in THF and treated with another equivalent of BuLi to yield a solution of $[C_5Cl_3(SLi)(Li)]Mn(CO)_3$ (**5b**), which, after addition of sulfur, gives $[C_5Cl_3(SLi)_2]Mn(CO)_3$ (**5c**). When each of the compounds **5a–c** is treated with $Au(PPh_3)Cl$, lithium is replaced by the $Au(PPh_3)$ fragment to yield the bi- and trimetallic compounds **6a–c** (eq. 4)).

Although these complexes could be isolated and characterized by their IR and NMR spectra (see Table 1), solutions usually turned black after several hours at r.t., presumably due to precipitation of gold metal. In an "old" $CDCl_3$ NMR solution of **6a** the disulfide $(OC)_3Mn[C_5Cl_4S\text{-}SCl_4C_5]Mn(CO)_3$ [20] and $AuPPh_3Cl$ can be identified. This observation parallels the reported decomposition of Fc—S—$AuPPh_3$ with HBF_4 to yield Fc—S—S—Fc [19] and the formation of $\{[C_5H_4(SAuPPh_3)]Fe\}_2(\mu\text{-})[C_5H_4SSC_5H_4]$ from $[C_5H_4SH]_2Fe$ and $[Au(PPh_3)]_3O^+BF_4^-$ [21].

The ^{31}P-NMR spectra always show rather broad absorptions for the sulfur-bound $Au(PPh_3)$ moieties, while the carbon bound $Au(PPh_3)$ group in **6b** as well as the other σ-metallated species reported here give sharp signals. This broadening might be an indication of a dynamic process of $Au(PPh_3)$ groups "jumping" between different thiolate groups, perhaps *via* dimeric



(Eq. 4)

intermediates with two gold fragments attached simultaneously to two different thiolate groups. Alternatively, any excessive Au(PPh$_3$)Cl left from the synthesis might attack the sulfur atom of an already aurated complex thus giving a diaurated species as it is well known from ferrocene or ruthenocene chemistry [12]. An indication of such a reaction is the elemental analysis (CHNS) of the crude reaction product of **6c**, which corresponds to a formulation as **6c***2 Au(PPh$_3$)Cl. Unfortunately, the solution instability of these compounds did not allow a variable temperature NMR study, as was possible with a benzenedithiolate complex of gold [17(c)], and therefore this interpretation has some speculative character, at least at present.

EXPERIMENTAL

All reactions were performed under dry nitrogen or argon, using Schlenkrohr techniques. Solvents were purified by standard methods and saturated with nitrogen. Reagents were commercially available and used without further purification. Organometallic starting materials were prepared as previously reported. NMR spectra were recorded at a JEOL GSX 270 instrument, using external H_3PO_4 as reference for ^{31}P-NMR spectra and the solvent signal of C_6D_6 as internal reference ($\delta = 128.0$ ppm) for ^{13}C-NMR spectra.

Tetrachloro(triphenylphosphinesilver)cymantrene [$C_5Cl_4Ag(PPh_3)$]Mn(CO)$_3$, **2b**

A solution of **1a** (420 mg, 1.00 mmol) in 20 cm^3 Et_2O is treated with BuLi solution (0.625 cm^3, 1.00 mmol) at -60°C for 15 min, before Ag(PPh$_3$)$_3$Cl (840 mg, 1.00 mmol) is added. The temperature is raised to ambient within 14 h. After the solvent is evaporated *in vacuo*, the residue is washed three times with 10 cm^3 pentane and once with 20 cm^3 Et_2O. The resulting off-white solid is extracted with 10 cm^3 CH_2Cl_2, the extract brought to dryness and the solid washed with 20 cm^3 pentane. After drying *in vacuo* a yield of 250 mg can be isolated, which according to its IR spectrum contains about 5% of an impurity identified as **1c**. IR monitoring of a CH_2Cl_2 solution of this product shows a continuous decrease of the CO bands of the Ag complex **2b** and a concomitant increase of the CO bands due to **1c**.

(tert. *Butylisonitrilegold*)*tetrachlorocymantrene* [$C_5Cl_4AuCN^tBu$]Mn(CO)$_3$, **2c**

A solution of **1a** (540 mg, 1.30 mmol) in 15 cm^3 Et_2O is stirred for 15 min at -78°C with BuLi solution (0.79 cm^3, 1.30 mmol). After addition of Au(CN^{t}Bu)Cl (400 mg, 1.30 mmol) stirring is continued for 1 h, before the temperature is raised to ambient, which leads to precipitation of a white solid. The solvent is stripped off *in vacuo* and the resulting residue is treated with CH_2Cl_2. The suspension is centrifuged, the precipitate discarded and the solution evaporated to dryness. The oily residue is taken up in Et_2O and chilled to -30°C, whereby a greyish powder precipitates: **2c** (710 mg, 88%). IR: $\nu(N{\equiv}C) = 2226$ cm^{-1} (Nujol). (Calc./Found): C, 24.2/25.1; H, 1.6/1.5; N, 2.3/2.3%.

Tetrabromo-triphenylphosphinogold-cymantrene [$C_5Br_4(AuPPh_3)$]Mn(CO)$_3$, **2d**

A solution of **1a** (242 mg, 0.40 mmol) in 20 cm^3 Et_2O is treated with BuLi solution (0.25 cm^3, 0.40 mmol) at -70°C. After five min, Au(PPh$_3$)Cl (200 mg, 0.40 mmol) is added, and the resulting red suspension is stirred for another 60 min at this temperature. Then the reaction mixture is brought to ambient temperature within 30 min and the solvent is evaporated *in vacuo*. The grey residue is extracted twice with 10 cm^3 CH_2Cl_2 each, and the dark red extract is evaporated to dryness again. After washing twice with 10 cm^3 pentane, the residue is taken up in Et_2O and filtered though silica gel. A bright yellow fraction is collected and evaporated to dryness. Yield 226 mg (58%). (Calc./Found): C, 32.1/32.2; H, 1.5/2.1%.

Reaction of **2d** *with* BuLi *and* Au(PPh$_3$)Cl

A solution of **2d** (89 mg, 0.09 mmol) in 10 cm^3 Et_2O is treated with BuLi solution (0.057 cm^3, 0.09 mmol) at −70°C, and after five min stirring with $Au(PPh_3)Cl$ (45 mg, 0.10 mmol). After 10 min at this temperature the cooling bath is removed and the mixture stirred for another 30 min at r.t. Then the ether is stripped off *in vacuo* and the residue is washed with 10 cm^3 pentane. (The pentane fraction contains, according to its IR spectrum, unreacted **2d** together with $[C_5Br_4H]Mn(CO)_3$. The residue is taken up in CH_2Cl_2, filtered and examined by IR spectroscopy: 75% **2d** and 25% **3b**.

Reaction of $[C_5Br_5]Mn(CO)_3$ *with* 4 *eq*. BuLi *and* $Au(PPh_3)Cl$

A solution of $[C_5Br_5]Mn(CO)_3$ (300 mg, 0.50 mmol) in 25 cm^3 Et_2O at −50°C is treated with BuLi solution (1.26 cm^3, 2.02 mmol), and, after 5 min stirring, with $Au(PPh_3)Cl$ (1.00 g, 2.02 mmol). After 30 min at this temperature, cooling is stopped, which leads to a colour change to dark brown. Ether is removed *in vacuo*, the residue washed with 10 cm^3 pentane and then extracted with CH_2Cl_2. After filtration, the solution is examined by spectroscopy (IR, ^{31}P-NMR): **1b, 2d, 3b** and $Au(PPh_3)Cl$.

Tetrachlorotributylphosphinegoldcymantrene $[C_5Cl_4(AuPBu_3)]Mn(CO)_3$, **2e**

A solution of **2a** (250 mg, 0.30 mmol) in 10 cm^3 toluene is treated with PBu_3 (77 cm^3, 0.30 mmol) with stirring for 20 min before it is evaporated *in vacuo* to leave a yellowish oil. According to its ^{31}P-NMR spectrum this oil only contains one species besides free PPh_3. Recrystallization from MeOH is possible, but leads to enormous losses in yield.

Trichlorobis(triphenylphospangold)cymantrene $[C_5Cl_3(AuPPh_3)_2]Mn(CO)_3$, **3a**

A solution of **1a** (270 mg, 0.64 mmol) in 5 cm^3 THF is treated with BuLi solution (4.0 cm^3, 6.40 mmol) at −78°C. After stirring for 5 min at this temperature, 20 cm^3 hexane is added and stirring is continued for another 10 min. When the precipitate has settled, the solution is siphoned off *via* a teflon cannula and discarded. The moist residue is washed with another portion of cold hexane, which is siphoned off again. The residue is taken up in 10 cm^3 cold Et_2O and treated with small amounts of $AuPPh_3Cl$ (total amount 635 mg, 1.28 mmol). The mixture is stirred for 1.5 h at −78°C, warmed immediately to r.t. and evaporated *in vacuo*. The precipitate is extracted with two portions of 10 cm^3 CH_2Cl_2, filtered, and the filtrate brought to dryness again. The residue is taken up in Et_2O and filtered through silica gel. The bright yellow eluate is evaporated *in vacuo* to leave an off-white powder. Yield 610 mg (78%). (Calc./Found): C, 43.2/42.9; H, 2.5/2.7%.

Tribromo-bis(triphenylphosphinogold)cymantrene $[C_5Br_3(AuPPh_3)_2]Mn(CO)_3$, **3b**

A solution of **1b** (242 mg, 0.40 mmol) in 20 cm^3 Et_2O at −70°C is treated with BuLi (0.50 cm^3, 0.80 mmol), and after five min stirring with $Au(PPh_3)Cl$ (396 mg, 0.80 mmol). The mixture is gradually warmed to −30°C within 3.5 h and then brought to ambient temperature. After evaporation of the solvent the residue is washed twice with 10 cm^3 pentane and then extracted twice with 10 cm^3 CH_2Cl_2. The combined extracts are brought to dryness *in vacuo* again. The residue is taken up in Et_2O and filtered through silica gel. The yellow-orange eluate is evaporated to dryness. Yield 220 mg (41%). (Calc./Found): C, 39.2/40.0; H, 2.2/2.4%.

Synthesis of $[C_5Cl_3(AuPBu_3)(Ni(PBu_3)_2Cl)]Mn(CO)_3$, **4**

A solution of **2a** (250 mg, 0.31 mmol) in 10 cm^3 toluene is treated with P^nBu_3 (77 mm^3, 0.31 mmol) under stirring for 20 min. The resulting yellow solution is treated with a solution of $Ni(PBu_3)_2(C_2H_4)$, obtained *in situ* from sodium dust reduction of $Ni(PBu_3)_2Cl_2$ in toluene under ethylene, at −78°C. The mixture is warmed to r.t. and stirred for another 2 h, when the solvent is stripped off *in vacuo*. Chromatography on silica gel (pentane/ether 5 : 1) gives an orange band, which is collected and evaporated to dryness. The resulting oil is dissolved in pentane and cooled to −30°C. After several days **4** crystallizes as red crystals. Yield: 132 mg, 35%. (Calc./Found): C, 43.9/43.9; H, 6.8/6.8%.

Tetrachloro(triphenylphosphinegoldmercapto)cymantrene $[C_5Cl_4(SAuPPh_3)]Mn(CO)_3$, **6a**

A solution of **5a** (90 mg, 0.24 mmol) in 10 cm^3 Et_2O is treated at −25°C with $Au(PPh_3)Cl$ (119 mg, 0.24 mmol) and then brought to r.t. within 1 h. Then an off-white precipitate is isolated and extracted with 2 cm^3 CH_2Cl_2. The extract is evaporated *in vacuo* to leave an off-white powder. Yield 165 mg (82%). (Calc./Found): C, 37.5/37.1; H, 1.8/2.0%.

Trichloro(triphenylphosphinegold) (triphenylphosphinegoldmercapto)cymantrene $[C_5Cl_3(AuPPh_3)(SAuPPh_3)]Mn(CO)_3$, **6b**

A solution of **5a** (208 mg, 0.55 mmol) in 12 cm^3 Et_2O is treated at −45°C with BuLi solution (0.36 cm^3, 0.58 mmol). While stirring is continued a brown precipitate forms. After 30 min, the resulting suspension is treated with $Au(PPh_3)Cl$ (542 mg, 1.47 mmol) and kept at this temperature for 1 h. Then the mixture is warmed to r.t. with continuous stirring for another hour. The solvent is stripped off *in vacuo*, the residue extracted with 5 cm^3 CH_2Cl_2 at -30°C and the extract filtered through silica gel. The filtrate is evaporated *in vacuo* to leave a gold-coloured residue. Yield 281 mg (40%). (Calc./Found): C, 42.1/43.0; H, 2.4/2.8; S, 2.5/2.5%.

Trichlorobis(triphenylphosphinegoldmercapto)cymantrene $[C_5Cl_3(SAuPPh_3)_2]Mn(CO)_3$, **6c**

A suspension of **5c** (140 mg, 0.37 mmol) in 10 cm^3 CH_2Cl_2 is treated at r.t. with $Au(PPh_3)Cl$ (356 mg, 0.73 mmol) and stirred for 2 h. After filtration the solvent is evaporated *in vacuo* to leave a yellowish-brown oily residue. After washing several times with pentane the oil solidifies. Chromatography on silica gel with CH_2Cl_2 yields a yellow band which is collected. Evaporation of the solvent and washing with 5 cm^3 pentane leaves a yellow powder. Yield 380 mg, 81%. (Calc./Found): C, 41.0/41.0; H, 2.3/2.9; S, 5.0/4.9%.

CONCLUSIONS

We have shown that using perhalogenated cyclopentadienyl manganese complexes allows the synthesis of trimetallic complexes with the cyclopentadienyl ligand acting as a π-ligand to one and as a σ-ligand to two other transition metals, either by the halogen–lithium exchange reaction followed by direct metallation or metallation of an intermediate thiolate or by oxidative addition of a cyclopentadienyl halogen bond to a Ni^0 phosphine moiety. Further studies will have to show if it is possible to achieve higher degrees of metallation by changing to other perhalogenated cyclopentadienyl complexes, other lithiation agents or other transition metal electro- or nucleophiles.

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