Maleonitriledithiolate Complexes of Au(III), Au(I), Pd(II) and Pt(II) Containing Neutral or Anionic Ligands

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Novel neutral or ionic complexes of gold(III) [Au(mnt)ClL] (L = tht(tetrahydrothiophene), PPh₃ or py), [Au(mnt)X₂]⁻ (X = Cl or Br) and [Au(mnt)-(LL)]⁺ (LL = bipy or phen), and neutral complexes of gold(I) [Au₂(mnt)LL] (L = PPh₃; LL = dpm((diphenylphosphino)methane) and of Pd(II) and Pt(II) [M(mnt)(LL)] (M = Pd, LL = bipy or phen; M = Pt, LL = phen or cod(1,5-cyclooctadiene)) have been prepared by using (mnt)SnMe₂ (mnt = 1,2-maleonitriledithiolate) as a precursor.

Introduction

Over the past two decades the great interest taken in 1,2-dithiolene complexes $[M(S_2C_2R_2)_n]^z$ (n = 2, 3; R = H, CN, CH_3, C_6F_5, *etc.*; z = 0, 1–, 2–, 3–) has determined the development of a large number of novel synthetic routes. This interest is multiplex and reaches from theoretical studies concerning the bonding to applications in very different fields, as may be seen from several reviews on this area [1].

Though complexes, which besides the 1,2-dithiolene group contain also other different ligands (*e.g.* CO, NO, PR_3, Py, η^5-C_5H_5) have been described, the main attention has been paid to the homoleptic complexes $[M(S_2C_2R_2)_n]^z$. Of the type $[M(s_2C_2-R_2)L_2]$ (M = Pd, Pt), for R = CN only the complexes with L = PPh_3 have been described [2]; a series of mixed 1,1-/1,2-dithiolene complexes $[M(mnt)-(dtc)]^z$ (dtc = dithiocarbamate, M = Pd, Pt, z = 1–; M = Au, z = 0) have furthermore been reported [3].
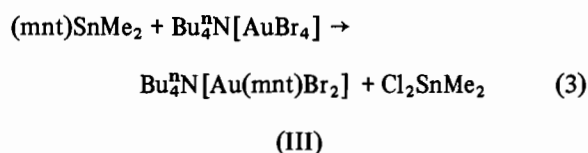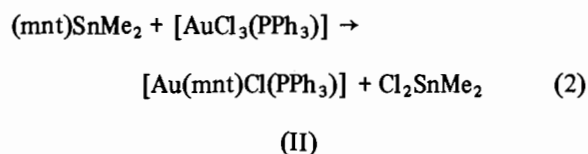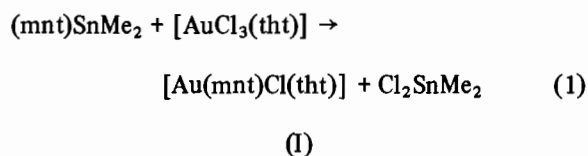
Herein we show how (mnt)SnMe₂ can be used for the preparation of heteroleptic Au(III), Pd(II) and Pt(II) complexes, some of which are unique and are not accessible by the classical reaction with Na₂(mnt). Amongst these are the only known halo- and olefine complexes as well as the first hitherto reported Au(I) derivatives.

(mnt)SnMe₂ has previously been employed for the synthesis of $[M(mnt)]_n$ (M = Cd, Hg) [4]. We use it in this area as a part of our more general research project on tin compounds as intermediate in the preparation of both inorganic and organometallic compounds [5].

Results and Discussion

Gold Complexes

The reaction of (mnt)SnMe₂ [4] with different gold(III) complexes $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) [6], $[AuCl_3(PPh_3)]$ [7] and $Bu_4^nN[AuBr_4]$ [8] in equimolecular ratios takes place according to the following exchange processes

$$(mnt)SnMe_2 + [AuCl_3(tht)] \rightarrow$$
$$[Au(mnt)Cl(tht)] + Cl_2SnMe_2 \qquad (1)$$
$$(I)$$

$$(mnt)SnMe_2 + [AuCl_3(PPh_3)] \rightarrow$$
$$[Au(mnt)Cl(PPh_3)] + Cl_2SnMe_2 \qquad (2)$$
$$(II)$$

$$(mnt)SnMe_2 + Bu_4^nN[AuBr_4] \rightarrow$$
$$Bu_4^nN[Au(mnt)Br_2] + Cl_2SnMe_2 \qquad (3)$$
$$(III)$$

If the first reaction (eqn. 1) is carried out [9] with Na₂(mnt) instead of (mnt)SnMe₂, a brown compound is obtained, which is different from the green [Au(mnt)Cl(tht)] (I). We were not able to characterise it, but its IR spectrum points to the presence of the anion $[Au(mnt)_2]^-$. The tendency to form this anion [10] can clearly be seen from process (4)

$$[AuCl_3(PPh_3)] + Na_2mnt + PPh_3 \longrightarrow$$

$$[Au(PPh_3)_2]^+[Au(mnt)_2]^- \quad (4)$$
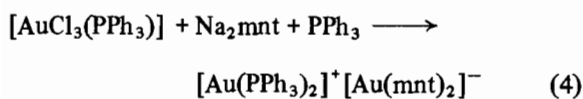
and also from the following reaction (5)

$$(5)$$
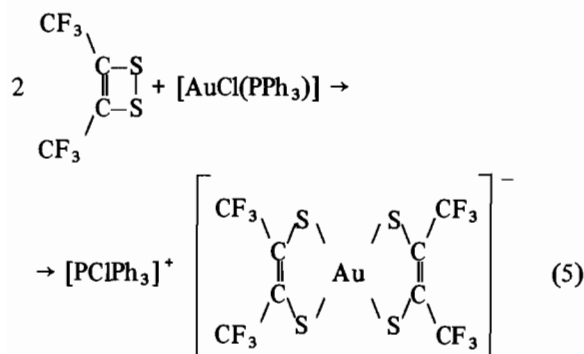
which leads to the formation of the homoleptic anionic species $[Au\{S_2C_2(CF_3)_2\}]^-$ [11].

Thus, the tin derivative $(mnt)SnMe_2$ opens a new route for the synthesis of 1,2-maleonitriledithiolate complexes, which cannot be obtained in reactions with $Na_2(mnt)$.

Reaction of (I) with PPh_3 leads to symmetrization (eqn. 6)

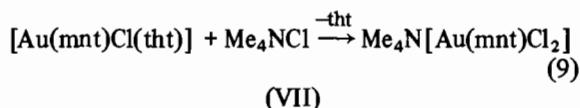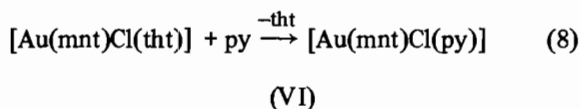$$2[Au(mnt)Cl(tht)] + 2PPh_3 \rightarrow$$

$$[AuCl_2(PPh_3)_2]^+[Au(mnt)_2]^- + 2\,tht \quad (6)$$

$$(IV)$$
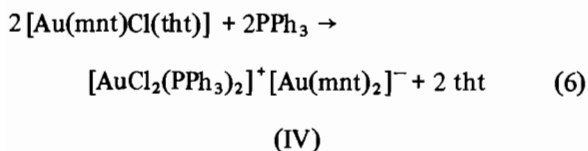
which affords complex (IV), a polymerization isomer of $[Au(mnt)Cl(PPh_3)]$ (II), whose physical properties (colour, melting point, conductivity, IR spectrum, *etc.*) are completely different from those of complex (II). Complex (IV) can partially be reduced with PPh_3 to give the previously described [10] mixed gold(I)–gold(III) complex $[Au(PPh_3)_2]^+[Au(mnt)_2]^-$ (V) (eqn. 7)

$$[AuCl_2(PPh_3)_2]^+[Au(mnt)_2]^- + PPh_3 \rightarrow$$

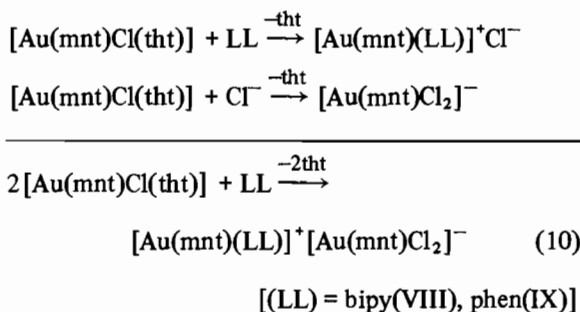$$[Au(PPh_3)_2]^+[Au(mnt)_2]^- + Cl_2PPh_3 \quad (7)$$
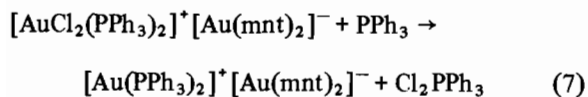
which can also directly be obtained by either reacting complex(I) with an excess of PPh_3, or by reacting complex(II) with PPh_3.

Other complexes can also be prepared by making use of the ready displacement of the tht ligand from gold(III) complexes [12]. Thus, the reaction of complex (I) with pyridine (py) or Me_4NCl gives rise to the replacement of the tht ligand, according to the following processes (eqns. 8 and 9),

$$[Au(mnt)Cl(tht)] + py \xrightarrow{-tht} [Au(mnt)Cl(py)] \quad (8)$$

$$(VI)$$

$$[Au(mnt)Cl(tht)] + Me_4NCl \xrightarrow{-tht} Me_4N[Au(mnt)Cl_2]$$
$$(9)$$

$$(VII)$$

leading to complexes similar to (I), (II) and (III). Moreover, the use of neutral bidentate ligands (LL), such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) yields compounds of the general formula $Au_2(mnt)_2Cl$ (LL), even if a 1:1 molar ratio is employed. The resulting complexes are 1:1 electrolytes (see Table I) which could be formulated as either $[Au(mnt)(LL)]^+[Au(mnt)Cl_2]^-$ or $[AuCl_2(LL)]^+[Au(mnt)_2]^-$. IR data (see further on) support the assignment of the first formulation. The process is therefore likely to take place according to the two step sequence (10)

$$[Au(mnt)Cl(tht)] + LL \xrightarrow{-tht} [Au(mnt)(LL)]^+Cl^-$$

$$[Au(mnt)Cl(tht)] + Cl^- \xrightarrow{-tht} [Au(mnt)Cl_2]^-$$

$$2[Au(mnt)Cl(tht)] + LL \xrightarrow{-2tht}$$

$$[Au(mnt)(LL)]^+[Au(mnt)Cl_2]^- \quad (10)$$

$$[(LL) = bipy(VIII), phen(IX)]$$

The second step has been confirmed (eqn. 9) in the preparation of $Me_4N^+[Au(mnt)Cl_2]^-$ (VIII).

Finally, the reaction between $(mnt)SnMe_2$ and the gold(I) complexes $[AuCl(PPh_3)]$ [13] and $[(AuCl)_2(dpm)]$ [14] (dpm = (diphenylphosphino)methane) leads to the synthesis of $[Au_2(mnt)(PPh_3)_2]$ (X) or, respectively, $[Au_2(mnt)(dpm)]_n$ (XI), which are the first gold(I) complexes containing a 1,2-dithiolene ligand. Complex (XI), which is insoluble in all the tested organic solvents, is thought to be a polymeric material.

Palladium and Platinum Complexes

The reaction of $(mnt)SnMe_2$ with $[PdCl_2(bipy)]$ [15], $[PdCl_2(phen)]$ [16], $[PtCl_2(phen)]$ [17] or $[PdCl_2(cod)]$ [18] (cod = 1,5-cyclooctadiene) take place according to the general process (eqn. 11)

$$(mnt)SnMe_2 + [MCl_2(LL)] \rightarrow$$
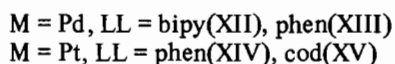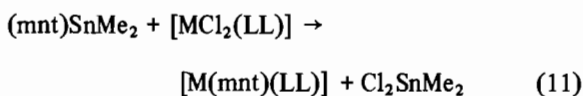
$$[M(mnt)(LL)] + Cl_2SnMe_2 \quad (11)$$

M = Pd, LL = bipy(XII), phen(XIII)
M = Pt, LL = phen(XIV), cod(XV)

TABLE I. Analytical and Physical Data for the Complexes.

Complexes		Analysis, (%) (Calc.)				Yield %	Colour	M.p. °C	Λ_M^a Ω^{-1} cm^2 mol^{-1}	M.W. (calc.)
		C	H	N	Au					
[Au(mnt)Cl(tht)]	(I)	20.85 (21.22)	1.75 (1.90)	6.08 (5.80)	42.74 (43.17)	67	green	181d	2	496(461)
[Au(mnt)Cl(PPh$_3$)]	(II)	42.28 (41.61)	2.48 (2.38)	4.47 (4.41)	31.70 (31.02)	70	green	172d	15.4	640(635)
Bu$_4$N$^+$[Au(mnt)Br$_2$]$^-$	(III)	32.27 (32.49)	4.87 (4.91)	5.45 (5.68)	27.08 (26.64)	77	brown	113	128	—
[AuCl$_2$(PPh$_3$)$_2$]$^+$[Au(mnt)$_2$]$^-$	(IV)	41.14 (41.61)	2.65 (2.38)	4.82 (4.41)	30.45 (31.02)	57	brown	184d	111	—
[Au(PPh$_3$)$_2$]$^+$[Au(mnt)$_2$]$^-$	(V)	44.08 (44.46)	2.52 (2.63)	4.67 (4.76)	32.60 (32.86)	90	brown	248d	87.5	—
[Au(mnt)Cl(py)]	(VI)	24.04 (23.93)	1.16 (1.12)	9.00 (9.30)	44.10 (43.60)	70	green	202d	1.5	b
Me$_4$N$^+$[Au(mnt)Cl$_2$]	(VII)	20.79 (19.93)	2.59 (2.51)	8.52 (8.71)	40.77 (40.84)	83	green	254d	142	—
[Au(mnt)(bipy)]$^+$[Au(mnt)Cl$_2$]$^-$	(VIII)	24.50 (23.98)	0.96 (0.89)	9.16 (9.32)	41.99 (43.70)	100	purple	235	120	—
[Au(mnt)(phen)]$^+$[Au(mnt)Cl$_2$]$^-$	(IX)	26.95 (25.95)	1.01 (0.87)	9.17 (9.08)	42.04 (42.56)	82	brown	290d	120	—
[Au$_2$(mnt)(PPh$_3$)$_2$]	(X)	44.63 (45.38)	3.07 (2.85)	2.64 (2.64)	37.93 (37.20)	61	yellow	185d	4.8	b
[Au$_2$(mnt)(dpm)]$_n$	(XI)	37.67 (37.92)	2.62 (2.41)	3.05 (3.04)	42.93 (42.74)	70	yellow	212d	12.4^c	b
[Pd(mnt)(bipy)]	(XII)	41.74 (41.63)	2.00 (2.07)	13.91 (13.59)	—	88	red	>300	b	b
[Pd(mnt)(phen)]	(XIII)	44.81 (44.97)	1.84 (1.89)	13.06 (13.22)	—	86	brown	>300	b	b
[Pt(mnt)(phen)]	(XIV)	37.34 (37.28)	1.61 (1.56)	10.83 (10.87)	—	86	red	>300	b	b
[Pt(mnt)(cod)]	(XV)	33.20 (32.50)	2.75 (2.73)	6.33 (6.32)	—	55	yellow	185d	1.3	b

^{a}Where not otherwise stated in acetone. ^{b}Not soluble enough for determination. ^{c}In dimethylformamide.

The reaction of the platinum cyclooctadiene complex (XV) with PPh$_3$ can be used for the preparation of the previously described complex [Pt(mnt)-(PPh$_3$)$_2$] [2]. The reaction with phen, however, is very slow, even in refluxing chloroform and complex (XIV) can therefore been more conveniently prepared by starting from the tin complex (mnt)-SnMe$_2$ (eqn. 11).

The insolubility of complexes (XII–XV) in organic solvents precluded the determination of their molecular weights. Only complex (XV) is soluble enough in acetone to measure its conductivity, which is very low.

The analytical results, yields and physical properties for the isolated complexes are collected in Table I.

IR Spectra

The presence of 1, 2 or 3 sometimes shouldered bands due to ν(CN) at *ca.* 2200 cm^{-1} can clearly be observed in the IR spectra of all the complexes (I–XV).

Of the three bands which normally appear in the 1600–1400 cm^{-1} region [at 1530–1500 (not to be seen, however, in the gold(I) complexes), 1500–1460 and 1460–1435 cm^{-1}], the higher energy absorption can tentatively be assigned to the perturbed (C=C) stretching, since this band is not observed in any of the complexes which contain other ligands (except phen). (Bu$_4^n$N)[Au(mnt)$_2$] shows also a strong band at 1505 cm^{-1}, whilst complexes of the type (Bu$_4^n$N)$_2$[M(mnt)$_2$] (M = Pd, Pt, Ni, Zn or Cu) exhibit two bands at approx. 1480 and 1460 cm^{-1} which, however, have not been assigned [19]. For (Et$_4$N)$_2$[Ni(mnt)$_2$] the vibration at 1485 cm^{-1} has been assigned to ν(C=C) [20].

The Au(I) complexes (X) and (XI) could have either structure (A) or (B)

(A)   (B)
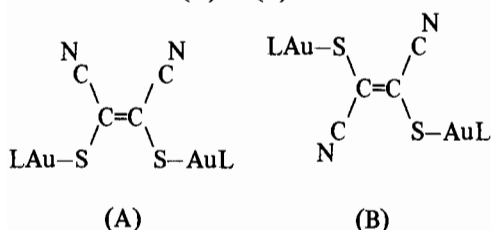
Structure (A) has been postulated for the complex [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$(mnt)] [21] because of the presence of a band which is assignable to the perturbed (C=C) stretching (in structure (B) ν(C=C) would not be IR active). In our case the absence of the band at 1530–1500 makes the choice between the two possible structures difficult, since other bands appearing at lower energies could be due to ν(C=C).

Towards 1150 cm^{-1} another generally sharp and strong band is observed in all the complexes. For [Ni(mnt)$_2$]$^{2-}$ this vibration has been assigned [20] to ν(C–C) + ν(C–S). It shows a shoulder in the ionic complexes [Au(mnt)(LL)] [Au(mnt)Cl$_2$] (VIII) and (IX), which could point to the presence of two different (mnt) groups. Complexes (IX), (XIII) and (XIV), which contain the ligand phen, show another band towards 1145 cm^{-1}, which in the spectra of complex (IX) can clearly be distinguished from the former. Complex (XI) exhibits a band at 1150 cm^{-1}, with a shoulder at 1140 cm^{-1} which could be due to the dpm ligand as may clearly be seen on comparing this spectrum with that of [(AuCl$_2$)-(dpm)].

The marked differences between the spectra of [AuCl$_2$(PPh$_3$)$_2$] [Au(mnt)]$_2$ (IV) and [Au(PPh$_3$)$_2$-] [Au(mnt)$_2$] (V) especially in the 1130–1100 and 550–450 cm^{-1} regions indicate that they are different species. For complex (IV) the presence of a very strong band at 542 cm^{-1} support a tentative *cis*-assignment for the cation [AuCl$_2$(PPh$_3$)$_2$]$^+$ if observations made for Pt(II) complexes [22] can be extended to gold(III) derivatives.

Several bands in the 400–300 cm^{-1} region in the spectra of maleonitriledithiolate complexes have been assigned to ν(M–S) vibrations coupled with several deformation modes [20]. For Bu$_4^n$N-[Au(mnt)]$_2$ the two absorptions at 355(m) and 330(m) cm^{-1} could probably also be assigned to this type of vibration. In complex (V) the two bands at 355(m) and 322(w) cm^{-1} confirm the presence of the anion [Au(mnt)$_2$]$^-$. These two absorptions are also observed in complex (IV) -though the first is broader whilst the second is stronger, possibly because of a overlapping of the ν(Au–S) and ν(Au–Cl) bands (see below). The differences in the spectra of [AuCl$_2$(PPh$_3$)$_2$] [Au(mnt)$_2$] (IV) and Me$_4$N-[Au(mnt)Cl$_2$] (VII) in this region preclude the possibility to formulate complex (IV) as [Au(mnt)-(PPh$_3$)$_2$] [Au(mnt)Cl$_2$].

Complexes Me$_4$N[Au(mnt)Cl$_2$] (VII), [Au(mnt)-(bipy)] [Au(mnt)Cl$_2$] (VIII) and [Au(mnt)(phen)]-[Au(mnt)Cl$_2$] (IX) show a strong assymmetric band at 340–335 cm^{-1}, assignable to ν(Au–Cl), thus confirming the presence of the anion [Au(mnt)Cl$_2$]$^-$. Furthermore, the three complexes present a band at 385 cm^{-1}, that is thought to be related to ν(Au–S). [Au(mnt)Br$_2$] (III) exhibits an absorption at 384 cm^{-1} along with a somewhat weaker one at 330 cm^{-1}, which could also be due to ν(Au–S). The latter is also observed — masking the vibration due to ν(Au–Cl) — in the spectra of complexes (VII)–(IX), though a shoulder is only to be seen for complex (VIII). Complex (IX) as well as (VIII) cannot be formulated as ionic, *i.e.* as [AuCl$_2$(phen)] [Au(mnt)$_2$] since ν(Au–Cl) for [AuCl$_2$(phen)]ClO$_4$ is located at 375 cm^{-1}, furthermore, there are also marked differences between the absorptions due to ν(C≡N) in

(VIII) and (IX) and the corresponding ones in $Bu_4^n N$-[Au(mnt)$_2$].

The chlorocomplexes (I), (II) and (VI) exhibit a strong or medium band at 345 cm^{-1}, assignable to ν(Au—Cl) along with weaker bands at *ca.* 380 and 320 cm^{-1}, which, in accordance with the above other assignments can be related to ν(Au—S).

The Pd and Pt derivatives (XII)—(XIV) show two or three bands in the 450—300 cm^{-1} region, which could be due to ν(M—S) coupled with several deformation modes.

Experimental

IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets or hexachlorobutadiene mulls between CsI windows. Conductivities were measured in 5×10^{-4} *M* solutions with a Philips PW 9501/01 conductimeter. Molecular weights were determined with a Hitachi Perkin-Elmer 115 osmometer. C, H, N analysis were performed with a Perkin-Elmer 240 microanalyzer. Au was determined by ashing the samples together with an aqueous solution of hydrazine.

[Au(mnt)Cl(tht)] (I)
0.74 g (0.25 mmol) of (mnt)SnMe$_2$ were added to a solution of 100 mg (0.25 mmol) of [AuCl$_3$-(tht)] in 20 ml of dichloromethane and stirred for 3 h. The filtered green solution was concentrated to 5 ml and 10 ml of ether was slowly added to precipitate complex (I).

[Au(mnt)Cl(PPh$_3$)] (II)
43.7 mg (0.15 mmol) of (mnt)SnMe$_2$ were added to a solution of 85 mg (0.15 mmol) of [AuCl$_3$-(PPh$_3$)] in 20 ml of dichloromethane, stirred for 1 h and filtered. The blue filtrate was concentrated to 5 ml and slow addition of 10 ml of hexane gave rise to the precipitation of complex (II).

$Bu_4^n N$[Au(mnt)Br$_2$] (III)
38 mg (0.13 mmol) of (mnt)SnMe$_2$ were added to a solution of 100 mg (0.13 mmol) of $Bu_4^n N$-[AuBr$_4$] in 20 ml of dichloromethane and stirred until the added compound was completely dissolved. The dark-brown solution was filtered and the filtrate was concentrated to 5 ml whereafter 10 ml of ether were slowly added to precipitate complex (III).

[AuCl$_2$(PPh$_3$)$_2$][Au(mnt)$_2$] (IV)
Addition of 57 mg (0.22 mmol) of PPh$_3$ to a solution of 100 mg (0.22 mmol) of complex (I) in 20 ml of dichloromethane led to a change of colour from green to brown. Complex (IV) precipitated slowly and was filtered off after 1 h.

[Au(PPh$_3$)$_2$][Au(mnt)$_2$] (V)
180 mg (0.69 mmol) of PPh$_3$ was added to a solution of 150 mg (0.33 mmol) of complex (I) in 20 ml of dichloromethane. The green solution turned brown and a brown precipitate was formed. The mixture was concentrated to 10 ml and complex (V) was separate by filtration.

Complex (V) can also be obtained by similarly reacting either complex (II) with PPh$_3$ (1:1) or complex (IV) with PPh$_3$ (1:1).

[Au(mnt)Cl(py)] (VI)
Addition of pyridine (0.02 ml, 0.25 mmol) to a solution of 100 mg (0.22 mmol) in 20 ml of dichloromethane led to the instantaneous precipitation of complex (VI).

Me$_4$N[Au(mnt)Cl$_2$] (VII)
20 mg (0.18 mmol) of Me$_4$NCl was added to a solution of 50 mg (0.11 mmol) of complex (I) in 10 ml of acetone and stirred for 7 h. The filtered solution was concentrated and 10 ml of ether were added to precipitate complex (VII).

[Au(mnt)(LL)][Au(mnt)Cl$_2$] (VIII–IX)
Bipy or phen (0.22 mmol) was added to a solution of 100 mg (0.22 mmol) of complex (I) in 20 ml of dichloromethane whereupon complex (VIII) or, respectively, (IX) precipitated instantaneously and could be separated by filtration.

[Au$_2$(mnt)(PPh$_3$)$_2$] (X)
29 mg (0.10 mmol) of (mnt)SnMe$_2$ were added to a solution of 100 mg (0.20 mmol) of AuCl(PPh$_3$) in 20 ml of dichloromethane. After 30 min, the solution was filtered, the filtrate was concentrated to 5 ml and 10 ml of ether were added to precipitate complex (X).

[Au$_2$(mnt)(dpm)]$_{\overline{n}}$ (XI)
34 mg (0.12 mmol) of (mnt)SnMe$_2$ were added to a solution of 100 mg (0.12 mmol) of [(AuCl)$_2$-(dpm)] in 20 ml of dichloromethane. The precipitated complex (XI) was separated by filtration after 1 h.

[Pd(mnt)(LL)] (XII–XIII)
A stoichiometric amount of (mnt)SnMe$_2$ was added to a suspension of [PdCl$_2$(LL)] (LL = bipy or phen) in 20 ml of acetone. The precipitated complexes (XII) or (XIII) were filtered off.

[Pt(mnt)(LL)] (XIV–XV)
A mixture (1.5:1) of (mnt)SnMe$_2$ and the platinum complex PtCl$_2$(LL) (LL = phen or cod) in 20

ml of acetone was refluxed for 10 h (for LL = phen) or, respectively, 5 h (for LL = cod) whereupon the suspensions were allowed to cool to room temperature and the respective complexes were separated by filtration.

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