Journal of Organometallic Chemistry, 141 (1977) 345—353

THE SYNTHESIS AND PROPERTIES OF DIARYLGOLDZINC CHLORIDES, DIPHENYLGOLDCADMIUM CHLORIDE, AND DIPHENYLGOLDMERCURY CHLORIDE

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(Received June 29th, 1977)

Summary

The arylation of carbonylgold chloride with diarylzinc compounds yields either triarylgoldzinc or diarylgoldzinc chlorides, depending on the reactant ratio and the nature of the aryl group. The same reactions with diphenylcadmium and diphenylmercury yield exclusively diphenylgoldcadmium chloride and diphenylgoldmercury chloride, respectively. The reactions of the products with *N,N,N',N'*-tetramethylethylenediamine and triphenylphosphine were studied.

Phenylgold has been obtained as a very unstable solid from diphenylgoldzinc chloride and diphenylgoldmercury chloride.

Introduction

In an earlier paper [1] we described the preparation of triarylgoldzinc compounds. These compounds were obtained from carbonylgold chloride (or gold trichloride) by treatment with an excess of a diarylzinc compound. When the same reactions are carried out with carbonylgold chloride using a 1/1 ratio of the reactants, colourless diarylgoldzinc chlorides are formed. The latter compounds are obtained exclusively, irrespective of the ratio of the reactants, when *ortho*-substituted diarylzinc compounds are used. With diphenylcadmium and diphenylmercury only diphenylgoldcadmium chloride and diphenylgoldmercury chloride are formed. In this paper we describe the preparation and characterization of diarylgoldmetal(II) chlorides (metal(II) = Zn, Cd, Hg).

Results

i. Reactions of diarylzinc compounds with carbonylgold chloride (Au(CO)Cl)

Upon gradually adding a solution of Au(CO)Cl in diethyl ether to a diphenylzinc solution in the same solvent at −40°C, a red precipitate of triphenylgoldzinc formed initially (eq. 1). When the addition of Au(CO)Cl was continued

$$Au(CO)Cl + 2Ph_2Zn \xrightarrow[-40^\circ C]{Et_2O} Ph_3AuZn\downarrow + PhZnCl + CO \qquad (1)$$

beyond a 1/2 molar ratio of Au(CO)Cl to Ph_2Zn, the precipitate gradually dissolved and a clear yellow solution resulted when the ratio reached one. Upon diluting the reaction mixture with an equal volume of pentane, a cream-coloured precipitate formed, which analyzed correctly for $Ph_2AuZnCl$. Surprisingly, this precipitate, when once obtained dry was only slightly soluble in common organic solvents. This contrasts with the behaviour of Ph_3AuZn which, although sparingly soluble in diethyl ether, dissolves readily in aromatic solvents and carbon disulfide. Di-*p*-tolylzinc reacts in a similar way with Au(CO)Cl, initially forming tri-*p*-tolylgoldzinc and finally giving cream-coloured di-*p*-tolylgoldzinc chloride. When Au(CO)Cl was treated with *ortho*-substituted diarylzinc compounds (aryl = *o*-tolyl, *o*-vinylphenyl, 2,6-dimethoxyphenyl) under the same conditions, no initial precipitates of triarylgoldzinc species were observed. From the clear solutions diarylgoldzinc chlorides were isolated by dilution with pentane. Under no conditions were triarylgoldzinc compounds formed.

ii. Reactions of diphenylcadmium and diphenylmercury with carbonylgold chloride

The reaction of Au(CO)Cl with diphenylcadmium in ether/toluene at - 50°C yielded a colourless precipitate of $Ph_2AuCdCl$ even when a large excess of Ph_2Cd was used (eq. 2). Under no conditions was Ph_3AuCd formed. Any excess of

$$Ph_2Cd + Au(CO)Cl \xrightarrow[-60^\circ C]{Et_2O/toluene} Ph_2AuCdCl + CO \qquad (2)$$

Ph_2Cd did not react, and could be washed out with ether.

Similarly, diphenylmercury reacted with Au(CO)Cl to give a precipitate of $Ph_2AuHgCl$. Again no Ph_3AuHg was formed, even when Ph_2Hg was used in excess. The properties of $Ph_2AuHgCl$ are rather surprising. It explodes violently in the dry state at temperatures as low as —20°C, producing biphenyl, metallic gold and phenylmercury chloride. These products indicate the initial presence of phenyl—gold bonds. The explosive character of this compound prevented full characterization of its properties.

Characterization of the diarylgoldmetal(II) chlorides

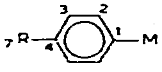
The diarylgoldmetal(II) chlorides have a very limited thermal stability. The zinc derivatives are less stable than the corresponding triarylgoldzinc compounds, and decompose within 5 min at 25°C in an inert atmosphere. The cadmium compound $Ph_2AuCdCl$ also decomposes rapidly at 25°C. The corresponding mercury derivative is the most labile, and is not stable above —20°C.

The thermal lability and insolubility of these compounds precluded molecular weight determinations even by cryoscopy in benzene. Although the solubility of these compounds is generally poor, those containing zinc are just sufficiently soluble to give NMR spectra. Table 1 shows the ^{13}C NMR data of diphenyl- and di-*p*-tolyl-goldzinc chloride in carbon disulfide.

Only four aromatic signals at positions characteristic of bridging phenyl groups (cf. ref. 1) are present. Furthermore the ^1H NMR spectra of $Ph_2AuZnCl$ in CS_2 and toluene-d_8 indicate the presence of only one type of aryl group, the *ortho*-

TABLE 1

^{13}C NMR RESONANCES OF $Ar_2AuZnCl$ [a]

	C(1)	C(2)	C(3)	C(4)	C(7)
$Ph_2AuZnCl$	146.7(146.7) [b]	132.1(132.0)	129.4(129.5)	127.6(127.3)	
p-$Tol_2AuZnCl$	147.8(147.5)	138.7(141.8)	127.5(128.2)	130.2(130.1)	22.6(22.7)

[a] In ppm relative to TMS, at −40°C. [b] In parentheses the equivalent positions for bridge-aryl in Ar_3AuZn.

proton absorptions of which are shifted to lower field, as for the bridging phenyl groups in Ph_3AuZn [1]. The IR spectra of the diarylgoldzinc chlorides show the presence of aryl groups bound to both gold and zinc. (Y-modes [2] 453 and 470 cm^{-1} (phenyl), 493 and 506 cm^{-1} (*p*-tolyl)).

The insolubility of $Ph_2AuCdCl$ in any suitable solvent precluded the recording of NMR spectra. The IR data, as in the case of the zinc derivatives, indicate the presence of two different phenylmetal bonds (Y-modes 450, 476 cm^{-1}, cf. Ph_2Cd 445 cm^{-1}, $PhAuCl_2$ 473 cm^{-1}). The ^1H-NMR spectrum of $Ph_2AuHgCl$ in pyridine-d_5 at −20 to −40°C shows two complex multiplets, at 7.2—7.7 ppm and 8.0—8.3 ppm, attributable to *meta* plus *para* protons and *ortho* protons, respectively. No ^{13}C NMR data could be obtained because of the low solubility and thermal instability of this compound. The IR bands observed for $Ph_2AuHgCl$ below 600 cm^{-1} do not coincide with those of Ph_2Hg or $PhHgCl$.

Reactions with nitrogen- and phosphorus-containing ligands

Since spectroscopy gives only limited information on the compounds under investigation their reactions were studied with the nitrogen-containing bidentate ligand TMED (*N,N,N',N'*-tetramethylethylenediamine) and the phosphorus-containing ligand Ph_3P. Diarylgoldzinc chlorides react with TMED to give 1/1 complexes $Ar_2AuZnCl \cdot TMED$. These complexes are no more thermally stable than the parent compounds, and so no molecular weight determinations could be made. The ^1H NMR spectrum of $Ph_2AuZnCl \cdot TMED$, recorded at −40°C in $CDCl_3$, showed splitting of the CH_3—N signal into 3 singlets with a 1/1/2 intensity ratio at 2.61, 2.55 and 2.49 ppm. The CH_2—N protons appeared as a singlet at 2.09 ppm. This contrasts with the results for $Ph_3AuZn \cdot TMED$ [1], for which no splitting of the CH_3—N signal was observed. Upon warming to 25°C, $Ph_2AuZnCl \cdot TMED$ decomposes and the ^1H NMR spectrum then shows CH_3—N and CH_2—N signals (both singlets) at 2.28 and 2.40 ppm, respectively, while the original signals have disappeared. The presence of magnetically inequivalent CH_3—N groups may indicate that the TMED ligand is not bound exclusively to either a zinc or a gold atom, but may occupy a bridging position between zinc and gold. No indications of ligand exchange in the temperature range −40 to 25°C were apparent from the NMR spectra. $Ph_2AuZnCl \cdot TMED$ was also made by treating a suspension of $Ph_2Zn \cdot TMED$ in diethyl ether with an ether solution of Au(CO)Cl. The product was identical with that obtained from $Ph_2AuZnCl$ and TMED.

When $Ph_2AuZnCl$ was treated with Ph_3P, no complex containing both gold and zinc could be isolated. Instead, a mixture of $PhAu \cdot PPh_3$ and $PhZnCl$ was obtained. The gold-containing complex was obtained by converting the PhZnCl into an insoluble zinc species by air oxidation. This behaviour towards Ph_3P is identical with that shown by Ph_3AuZn [1].

When TMED was added to a suspension of $Ph_2AuCdCl$ in diethylether, colourless $Ph_2AuCdCl \cdot TMED$ was formed, which is a little more soluble than the parent compound. Again, the thermal stability was not improved. The ^1H NMR spectrum of this complex shows only two singlet signals of the TMED ligand (CH_3—N at 1.90; CH_2—N at 1.69 ppm in $CDCl_3$ solution) in contrast to the four signals of the $Ph_2AuZnCl \cdot TMED$ complex. This complex also decomposes at 25°C, and the ^1H NMR spectrum shows a new set of TMED signals at 2.45 and 2.52 ppm (CH_3—N and CH_2—N respectively) and none of the original signals.

Treatment of $Ph_2AuCdCl$ with an equimolar amount of Ph_3P in ether yielded a colourless precipitate of PhCdCl, and from the clear supernatant liquid $PhAu \cdot PPh_3$ was obtained quantitatively by evaporation of the solvent (eq. 3).

$$Ph_2AuCdCl + Ph_3P \xrightarrow{Et_2O} PhAu \cdot PPh_3 + PhCdCl \tag{3}$$

The behaviour of $Ph_2AuHgCl$ towards TMED and Ph_3P differs from that of its zinc and cadmium analogs. The addition of TMED to a suspension of $Ph_2AuHgCl$ in ether at —50°C yielded a light-brown, insoluble compound which, according to elemental analysis, contains much more gold and much less mercury and TMED than would correspond with either $Ph_2AuHgCl$ or its TMED complex. If the nitrogen is taken as TMED and the mercury as PhHgCl, the analytical data indicate that the compound consists of PhAu containing about 15 mol-% TMED and 9 mol-% PhHgCl.

The precipitate, which could not be purified further, exploded upon heating to 60°C. The decomposition into biphenyl and metallic gold began even at temperatures little above 0°C. The ethereal solution slowly deposited metallic gold, and after decomposition was found to contain PhHgCl, TMED and biphenyl. We interpret these results in terms of initial complexation of $Ph_2AuHgCl$ with TMED, followed by rapid breakdown of the initial complex into PhAu, PhHgCl, and TMED (eq. 4).

$$Ph_2AuHgCl + TMED \xrightarrow[-50^\circ C]{Et_2O} Ph_2AuHgCl \cdot TMED \rightarrow PhAu + PhHgCl + TMED \tag{4}$$

The reaction of $Ph_2AuHgCl$ with Ph_3P took a very different course. Depending on the amount of Ph_3P added, either $AuCl \cdot PPh_3$ or $AuCl \cdot 2PPh_3$ was formed, together with Ph_2Hg (eq. 5). Complexes of the type $AuX \cdot 2PPh_3$ are

$$Ph_2AuHgCl + nPPh_3 \xrightarrow[0^\circ C]{Et_2O} Ph_2Hg + AuCl \cdot nPPh_3 \tag{5}$$

$(n = 1, 2)$

known [3] but uncommon. Nesmeyanov et al. obtained $AuBF_4 \cdot 2PPh_3$ upon adding Ph_3P to ferrocenylgold tetrafluoroborate complexes [4].

Some further reactions of arylgoldzinc compounds

Since it is possible to synthesize Ar_3AuZn from $Ar_2AuZnCl$ and Ph_2Zn and, vice versa, $Ph_2AuZnCl$ is obtained from Ph_3AuZn and Au(CO)Cl, we tried to prepare mixed Ar_3AuZn compounds by treating ditolylzinc with diphenylgoldzinc chloride. However, the red compounds formed contained tolyl and phenyl groups in amounts governed only by the ratio of the reactants (eq. 6). The partition of groups between the bridging and terminal aryl positions in the triarylgoldzinc dimer [1] is purely statistical as was apparent from ^1H NMR data. Obviously, fast exchange reactions occur.

$$n\mathrm{Ph_2AuZnCl} + m\mathrm{Tol_2Zn} \xrightarrow[-40^\circ\mathrm{C}]{\mathrm{Et_2O}} n\mathrm{Ph}_n\mathrm{Tol}_m\mathrm{AuZn} + (m-n)\mathrm{Ph}_{2/3n}\mathrm{Tol}_{2/3m}\mathrm{Zn} + n\mathrm{Ph}_{1/3n}\mathrm{Tol}_{1/3m}\mathrm{ZnCl} \qquad (6)$$

$(m + n = 3, m > n)$

Reaction at −60°C of pure Ph_3AuZn in Et_2O/toluene with Au(CO)Cl afforded a yellow solution and an off-white precipitate, and the latter proved to be $Ph_2AuZnCl$. From the clear solution a yellow precipitate, possibly (impure) PhAu, was obtained by adding pentane (eq. 7). After washing with ether and drying, the yellow precipitate formed in this reaction exploded at −70°C when touched with a spatula; and PhPh and gold(0) were formed. It is clear that the properties of phenylgold differ markedly from those of phenylsilver [5].

$$\mathrm{Ph_3AuZn} + \mathrm{Au(CO)Cl} \rightarrow \mathrm{Ph_2AuZnCl} + \mathrm{PhAu} + \mathrm{CO} \qquad (7)$$

Discussion

Table 2 summarizes the reactions of Au(CO)Cl with the diphenyl compounds of the Group IIB metals and the coordination behaviour of the products.

As mentioned earlier, the full characterization of the diarylgoldmetal(II) chlorides is hampered by their insolubility and their thermal lability. The reactions with nitrogen- and phosphorus-containing ligands provided indirect information about the molecular structures. A structure containing the units shown in Fig. 1 is in accord with the data available.

This proposition accounts for the fact that both phenyl groups in $Ph_2AuZnCl$ are equivalent and bridging, as suggested by the ^{13}C NMR spectral data. The

TABLE 2

REACTIONS OF Au(CO)Cl WITH COMPOUNDS Ph_2M(M=Zn, Cd, Hg) AND COORDINATION BEHAVIOUR OF THE REACTION PRODUCTS

Products of the reaction $x Ph_2M + y Au(CO)Cl$	Reaction of the products with	
	Ph_3P	TMED
Ph_3AuZn (dec. 130°C) $x/y \geq 2$ M = Zn	$PhAu \cdot PPh_3 + Ph_2Zn$	$Ph_3AuZn \cdot TMED$
$Ph_2AuZnCl$ (dec. 25°C) $x/y = 1$ M = Zn	$PhAu \cdot PPh_3 + PhZnCl$	$Ph_2AuZnCl \cdot TMED$
$Ph_2AuCdCl$ (dec. 120°C) $x/y \geq 1$ M = Cd	$PhAu \cdot PPh_3 + PhCdCl$	$Ph_2AuCdCl \cdot TMED$
$Ph_2AuHgCl$ (expl. dec. −20°C) $x/y \geq 1$ M = Hg	$AuCl \cdot PPh_3$ or $AuCl \cdot 2PPh_3 + Ph_2Hg$	PhAu + PhHgCl + TMED

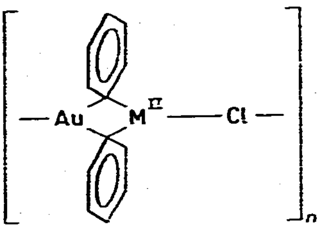


Fig. 1.

behaviour of $Ph_2AuZnCl$ and $Ph_2AuCdCl$ towards TMED and Ph_3P and the different behaviour of $Ph_2AuHgCl$ towards the same ligands can also be rationalized in terms of this picture. Since there are gold—phenyl and gold—chlorine interactions in these compounds, reaction with Ph_3P may cleave either of these bonds, depending on the Group IIB metal present in the compound. Clearly, the gold—phenyl bond is cleaved in $Ph_2AuHgCl$ and the gold—chlorine bond in $Ph_2AuZnCl$ and $Ph_2AuCdCl$. This behaviour runs parallel to the affinity of the group IIB metals for chlorine, as expressed by the metal—chlorine bond strengths in diatomic metal—chlorine molecules [6] (Zn—Cl 54.7 kcal mol^{-1}; Cd—Cl 49.9 kcal mol^{-1}; Hg—Cl 24 kcal mol^{-1}). The proposed structural picture contains three-coordinate gold(I). Although gold(I), like copper(I) and silver(I) is normally two-coordinate and *sp*-hybridized, three-coordination does occur for these metals as exemplified by the equatorial copper atoms in the $(2\text{-}Me_2NC_6H_4)_4Cu_6Br_2$ cluster [7] and the $(5\text{-}Me\text{-}2\text{-}Me_2NCH_2C_6H_3)_4Cu_4$ cluster [8].

Experimental

Unless stated otherwise, experiments were carried out under dry, oxygen-free nitrogen. Solvents were purified and stored under nitrogen. Solvents, solutions and liquid reagents were handled by syringes. Infrared investigations were carried out using a Perkin—Elmer 457 double beam grating spectrometer. Spectra were recorded between 4000 and 250 cm^{-1} on Nujol suspensions between polyethylene films or KBr discs; polystyrene was used for calibration. Frequencies given are believed to be accurate within 3 cm^{-1}. Samples were cooled to 0°C by blowing evaporating liquid nitrogen over their surfaces. NMR spectra were recorded using Varian A-60, EM360, XL100, or CFT-20 spectrometers. The ^1H values are believed to be accurate within 2 Hz, ^{13}C values within 0.1 ppm.

Decomposition temperatures (±5°) and melting points (±1°) were determined on a Kofler Heizbank. The temperatures given refer to immediate black colouration or, when indicated, to the time after which blackening was first observed. Analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, under supervision of Mr. W.J. Buis. Analysis of these extremely labile and reactive compounds involved great difficulties, especially the determination of carbon and hydrogen, which gave erratic results. Only the values for the metals and the other hetero-atoms involved are given.

Diphenylzinc was prepared by the Grignard route according to ref. 9. Diphenylcadmium was prepared from phenyllithium and cadmium bromide as described by Wittig [10]. Diphenylmercury was made by the Grignard route [11]. Carbonylgold chloride was prepared from $AuCl_3$ and carbon monoxide [12].

Synthesis and reactivity of diarylgoldzinc chloride compounds

Diphenylgoldzinc chloride. Slow addition of an ether solution of Au(CO)Cl to an equimolar amount of Ph_2Zn in ether at —40°C initially afforded a red precipitate of Ph_3AuZn, which disappeared again when the total amount of gold salt had been added. From the yellow solution, $Ph_2AuZnCl$ was isolated by addition of an equal volume of pentane. The off-white, sometimes slightly brown precipitate which formed was separated by decantation and washed with ether (3 × 50 ml) and pentane (50 ml). The product was dried at —20°C/0.1 mmHg. Preparations were carried out on a 1 mmolar scale, giving yields of about 50%. Decomposition: 65°C (1 sec), 25°C (5 min). Analysis: Found: Au, 42.7; Cl, 6.8; Zn, 14.0. $C_{12}H_{10}AuZnCl$ calcd.: Au, 43.58; Cl, 7.84; Zn, 14.46%. Ratio Au/Zn: 0.99;

Bis(p-tolyl)goldzinc chloride. The preparation was carried out as described for $Ph_2AuZnCl$, but only about 1/10th of the volume of pentane was needed for precipitation. Decomposition: 100°C (1 sec), 35°C (5 min). Analysis: Au, 41.3; Cl, 7.1; Zn, 12.9. $C_{14}H_{14}AuZnCl$ calcd.: Au, 41.03; Cl, 7.39; Zn, 13.62%. Ratio Au/Zn: 1.06.

Impure, cream-coloured bis(2,6-dimethoxyphenyl)goldzinc chloride precipitated in the reaction of 2.7 mmol of $(2,6\text{-diMeOPh})_2Zn$ with 0.8 mmol of Au(CO)Cl. The product decomposed at 190°C (1 sec), 25°C (5 min). Green 2-MeOPhAuZnCl_2 was obtained from equimolar amounts of Au(CO)Cl and 2-MeOPhZnCl in ether or toluene. Decomposition: 25°C (1 sec). Analysis: Found: Au, 40.6; Cl, 12.9; Zn, 13.4. $C_7H_7AuZnCl_2O$ calcd.: Au, 40.25; Cl, 14.49; Zn, 13.36%. A grey product, decomposing above —20°C was obtained from equimolar amounts of Au(CO)Cl and $o\text{-Tol}_2Zn \cdot 2THF$ in ether. Addition of PPh_3 to this product did not give the compound $o\text{-TolAu} \cdot PPh_3$. Grey, impure (according to elemental analysis) $(o\text{-VinPh})_2AuZnCl$ was obtained by addition of pentane to the clear reaction mixture of equimolar amounts of Au(CO)Cl and $(o\text{-VinPh})_2Zn$ in ether. The product decomposed at 130°C.

Reaction of diphenylgoldzinc chloride with TMED. A precipitate with composition $Ph_2AuZnCl \cdot TMED$ was obtained by addition of pure TMED to an equimolar amount of $Ph_2AuZnCl$ in ether solution at —40°C. The grey-white product, after washing with ether and drying, analyzed as follows: Found: Au, 37.0; Cl, 4.6; N, 4.4; Zn, 11.2. $C_{18}H_{26}AuZnClN_2$ calcd.: Au, 34.66; Cl, 6.24; N, 4.93; Zn, 11.51%. Ratio Au/Zn: 1.09. Decomposition: 50°C (1 sec). The same compound was obtained by a low-temperature addition of 1 equivalent of Au(CO)Cl to a suspension of $Ph_2Zn \cdot TMED$ in ether.

Reaction of diphenylgoldzinc chloride with triphenylphosphine. Addition of an ether solution of PPh_3 to a solution containing an equimolar amount of $Ph_2AuZnCl$ (i.e. to the clear yellow mixture of Ph_2Zn and Au(CO)Cl in a 1/1 molar ratio in ether/toluene) gave a clear colourless mixture. Dry air was bubbled through for 15 min and the resulting clear solution containing $PhAu \cdot PPh_3$ was separated from the deposit. Evaporation of the solvent yielded colourless $PhAu \cdot PPh_3$ (m.p. 164°C), with an IR spectrum superimposible on that of an authentic sample.

Exchange reactions of diarylgoldzinc chlorides. Red precipitates of Tol_mPh_n-AuZn were obtained by addition of known quantities of Tol_2Zn to $Ph_2AuZnCl$ in ether/toluene solution (that is to the crude reaction mixture containing the latter compound). The precipitates obtained were purified as described for Ph_3AuZn.

Reaction of triphenylgoldzinc with carbonylgold chloride. A solution of Au(CO)Cl (26 mmol) in toluene (100 ml) was slowly added to an equimolar amount of Ph_3AuZn in toluene (350 ml) at —60°C. The yellow solution gradually turned slightly brown and a precipitate formed. After 2 days at —70°C (a thin gold mirror had formed) the solution was decanted. The solid residue was $Ph_2AuZnCl$ (IR-comparison). An equal volume of pentane was added to the decanted solution to give a yellow precipitate. After washing with ether (3 × 25 ml) and pentane (2 × 25 ml) at —60°C, the dried product exploded at —70°C to give PhPh and gold(0) upon attempted sampling. Analysis of the decomposed product points towards impure PhAu. Found: Au, 75.4; Cl, 2.2; Zn, 5.0; calcd.: Au, 71.86; Cl, 0; Zn, 0%.

Synthesis and reactivity of diphenylgoldcadmium chloride

Diphenylgoldcadmium chloride. To a suspension of Ph_2Cd in ether was added an equimolar or smaller amount of Au(CO)Cl in toluene at —40 to —60°C. A yellow solution formed above the suspension. The supernatant was decanted after 90 min stirring and the solid was washed three times with ether and once with pentane at —40°C. After drying (—20°C/0.1 mmHg) a white material was obtained, sensitive to air and water and decomposing at 120°C. Because of its insolubility, even in strongly coordinating solvents, recrystallization was impossible. The same material was obtained as a white precipitate from a homogeneous reaction of Ph_2Cd with Au(CO)Cl (2 mmol) in 500 ml of 1/1 ether toluene mixture. Analysis: Found: Au, 36.8; Cd, 21.7; Cl, 8.3. $C_{12}H_{10}AuCdCl$ calcd.: Au, 39.47, Cd, 22.52; Cl, 7.1%. Ratio Au/Cd: 0.97.

Reaction of diphenylgoldcadmium chloride with triphenylphosphine. Addition of a solution of PPh_3 in ether to a suspension of an equimolar amount of $Ph_2AuCdCl$ in ether/toluene caused no visible change. $PhAu \cdot PPh_3$ was obtained from the clear supernatant liquid by evaporation of the solvents. The solid left after the decantation consisted of PhCdCl. When the reaction was repeated with PPh_3 and $Ph_2AuCdCl$ in a 2/1 ratio, $PhAu \cdot PPh_3$ was isolated from the clear supernatant solution, as was shown by its IR spectrum. The white solid analyzed this time for $PhCdCl.PPh_3$ after three washings with ether. Analysis: Found: Cd, 23.9; Cl, 7.2; P, 5.3; Au, <1. $C_{24}H_{20}CdClP$ calcd.: Cd, 23.07; Cl, 7.28, P, 6.36, Au, 0%.

Reaction of diphenylgoldcadmium chloride with TMED. A white product with the composition $Ph_2AuCdCl \cdot TMED$ was obtained when 1 equivalent of TMED was added at —40°C to a suspension of $Ph_2AuCdCl$ in ether/toluene. The solid obtained by decantation of the supernatant solution and washing with toluene (1 ×), ether (3 ×), and pentane (1 ×) was dried at 0°/0.1 mm. Analysis: Found: Au, 32.1; Cd, 18.2; Cl, 5.6; N, 3.2. $C_{18}H_{26}AuCdClN_2$ calcd.: Au, 32.01, Cd, 18.27; Cl, 5.76; N, 4.55%.

Synthesis and reactivity of diarylgoldmercury chloride

Diphenylgoldmercury chloride. A solution of Au(CO)Cl (110 mg, 0.4 mmol) in ether (90 ml) was slowly added to a solution of Ph_2Hg (450 mg, 1.3 mmol) in ether (30 ml) at —40°C. An off-white precipitate was formed. After 3 h at —50°C the precipitate was collected and washed three times with ether/pentane 1/1. The slightly brown precipitate obtained after drying was explosive at 120°C. The thermal stability diminished markedly with time; after one day at —70°C, decomposition took place at 20°C. The product was analyzed by allowing a weighed portion (all of which was recovered) to explode under controlled conditions. Analysis: Found: Au, 33.0; Hg, 29.2. $C_{12}H_{10}AuHgCl$ calcd.: Au, 33.54; Hg, 34.16%. Ratio Au/Hg: 1.15.

Reaction of diphenylgoldmercury chloride with triphenylphosphine. $AuCl \cdot 2PPh_3$ was formed by the addition of 2 equivalents of PPh_3 in ether to the crude product from Au(CO)Cl (4.0 mmol) and Ph_2Hg (4.0 mmol) at —10°C. (m.p. 178°C, dec. >180°C). Analysis: Found: Au, 26.0; P, 7.6. $C_{36}H_{30}AuP_2Cl$ calcd.: Au, 26.02; P, 8.18%.

Reaction of diphenylgoldmercury chloride with TMED. TMED (6 mmol) was added to the reaction product of Au(CO)Cl (3 mmol) and Ph_2Hg (3 mmol) in ether at —50°C. The buff-coloured product ($Ph_2AuHgCl$) turned gradually light-brown. After 2 h the solid was washed with ether (2 × 50 ml). The analysis of the light-brown product pointed to a mixture with composition $PhAu/PhHgCl \cdot TMED$, 11/1. PhHgCl, PhPh, gold(0) and TMED were present in the washing solutions. Attempted preparation of pure PhAu by addition of an Au(CO)Cl solution (4 mmol) in toluene to a solution of Ph_2Hg (3.2 mmol) and TMED (4 mmol) in ether at —30°C gave a brown precipitate, which turned purple during washing with ether (6 × 30 ml) at —70°C. Addition of $CHCl_3$ caused an explosion.

Acknowledgement

This investigation was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

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