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Ortho-nitrophenyl Complexes of Gold(III)

J. VICENTE*, M. T. CHICOTE, A. ARCAS and M. ARTIGAO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Murcia, Spain

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Introduction

Many organogold complexes have been prepared using Grignard or organolithium reagents [1], as well as organothallium [2] or organotin [3] complexes. We have recently shown that organomercury compounds can also be used for the synthesis of organogold(III) complexes which are inaccessible through other routes [4]. Many authors have used organomercurials in order to prepare organometallic compounds of other elements [5] and also of gold(I) [6]. We therefore thought it of interest to know how useful could organomercurials be in the synthesis of gold(III) complexes.

To test the method we chose a group such as *ortho*-nitrophenyl, which is difficult to bond to a metallic atom due to the unstability of the corresponding organolithium derivative [7] that has only scarcely been used [8]. The interest of preparing nitrophenyl organometallics is well documented, and the methods used are good examples of how the difficulties in the synthesis of organometallics can be overcome by choosing the proper intermediates [9–22]. In any case, this is the first report of the use of organomercurials in the synthesis of nitrophenyl complexes.

On the other hand it is known that *ortho* substituents exert a profound influence on the stability of arylmetal complexes [23–31] and this fact explains the great number of such complexes and the advances in the organometallic chemistry of many elements promoted by such special stability.

Our continuing interest in the synthesis of metallacycle complexes [3, 4, 32] relates to the possibility of the *ortho*-nitrophenyl group acting as a new type of chelate ligand to give a five-membered ring metallacycle. Although there is no evidence of such type of coordination in the complexes reported here, we have prepared some palladium(II) complexes where the metallacycle is present [33]. In the light of these results we continue in our attempts to obtain similar findings in the chemistry of gold(III).

Results and Discussion

The reactions between $[HgR_2]$ and $Me_4N[AuCl_4]$ give, after stirring for respectively 30 or 65 hr in refluxing acetone, the anionic complexes $Me_4N[AuR_2Cl_2]$ (R = o-$O_2NC_6H_4$ (I), 2-H_3C, 6-$O_2NC_6H_3$ (II). The reaction with $[Hg(C_6H_5)_2]$ in the same conditions gives metallic gold.

$$Me_4N[AuCl_4] + 2[HgR_2] \rightarrow Me_4N[AuR_2Cl_2] + 2[HgRCl]$$

The i.r. spectra of the complexes show two strong bands at 280, 300 cm^{-1} (I) and 285, 305 cm^{-1} (II) which can be assigned to $\nu(AuCl)$ (A_1) and $\nu(AuCl)$ (B_1) for a *cis*-geometry (C_{2v}). A *trans*-geometry (D_{2h}) would give just a band (B_{2u}) in the region 340–360 cm^{-1} due to the lower *trans*-influence of chloro with respect to the phenyl group [2b, 34, 35].

The *cis*-organometallic gold(III) complexes reported $[Au(CH_3)_2Cl_2]^-$ [36] $[Au(C_6F_5)_2Cl_2]^-$, $[Au(C_6F_3H_2)_2Cl_2]^-$ [2b] and $[Au(2,2'\text{-}C_{12}H_8)Cl_2]^-$ [3] also show two bands in their i.r. spectra at 268, 281; 310, 330; 315, 320 and 272, 316 cm^{-1} respectively.

^1H n.m.r. of complex (II) shows a multiplet centered at 7.18 p.p.m. (6H, phenyl protons) and two singlets at 3.09 p.p.m. (12H, $N(CH_3)_4$) and 2.52 p.p.m. (6H, H_3C-Ph).

When suspensions of complexes (I) or (II) in dichloromethane are treated with PPh_3 (1:1), suspensions of Me_4NCl and solutions containing $[Au(o\text{-}O_2NC_6H_4)_2Cl(PPh_3)]$ (III) or $[Au(2\text{-}H_3C, 6\text{-}O_2NC_6H_3)_2Cl(PPh_3)]$ (IV) are obtained.

$$Me_4N[AuR_2Cl_2] + PPh_3 \rightarrow [AuR_2Cl(PPh_3)] + Me_4NCl$$

R = o-$O_2NC_6H_4$ (III), 2-H_3C, 6-$O_2NC_6H_3$ (IV)

When pyridine is used complex (I) reacts similarly to give the complex $[Au(o\text{-}O_2NC_6H_4)_2Cl(py)]$ (V), but even if an excess of the ligand is used a mixture of (I) and (V) is always isolated, which can be separated due to the better solubility of (V) in diethyl ether.

The three neutral complexes present a medium band at 320 (III), 310 (IV) and 315 (V) cm^{-}. If complexes (III)–(V) were of *trans*-geometry we should expect in (V) $\nu(AuCl)$ *trans* to pyridine at

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*Author to whom correspondence should be addressed.

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higher frequency than ν(AuCl) *trans* to phosphine in (III) due to the lower *trans*-influence of the pyridine ligand. In addition ν(AuCl) *trans* to pyridine has been assigned at 363 cm^{-1} in $[Au(CN)_2Cl(py)]$ [37].

For these reasons we assign the bands observed in the 310–320 cm^{-1} region to ν(AuCl) *trans* to the phenyl rings and then a *cis*-geometry for complexes (III)–(V).

In fact, complex (IV) shows in its ^1H n m.r. spectra a multiplet centered at 7 62 p p.m. (21H, phenyl rings) and two singlets at 2.69 (3H) and 2.18 p.p.m. (3H) corresponding to the two different *o*-methyl groups.

All complexes are thermally stable in the solid state and in solution, as well as towards atmospheric moisture and daylight.

Experimental

cis-*$Me_4N[Au(o\text{-}O_2NC_6H_4)_2Cl_2]$ (I)*

To a solution of $Me_4N[AuCl_4]$ (139 mg, 0.34 mmol) in acetone (40 ml) $[Hg(o\text{-}O_2NC_6H_4)_2]$ [17] (310 mg, 0 7 mmol) was added and the mixture refluxed for 30 h. Concentration of the solution (to 5 ml) and slow addition of diethyl ether (30 ml) gave (I) (184 mg, 92% yield) as a pale yellow solid. M p. 186 ℃, Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (3.41 × 10^{-4} *M* in acetone solution). Analytical data. % Found: C 32.82, H: 3.50, N 7.00, Au· 33.30. $C_{16}H_{20}N_3Cl_2O_4Au$ requires C· 32.78, H: 3.44, N. 7.17, Au 33.60.

cis-*$Me_4N[Au(2\text{-}H_3C, 6\text{-}O_2NC_6H_3)_2Cl_2]$ (II)*

A solution of $Me_4N[AuCl_4]$ (234 mg, 0 57 mmol) and $[Hg(2\text{-}H_3C, 6\text{-}O_2NC_6H_3)_2]$ (533 mg, 1.13 mmol) in acetone (50 ml) was refluxed for 65 h, filtered and concentrated until a white solid appeared [(I) + unreacted mercurial], which was filtered. To the solution diethyl ether was added and the precipitated solid filtered and washed with methanol and diethyl ether to give (II) (295 mg, 42% yield) as a white solid. M.p. 200 ℃(d). Λ_M =108 Ω^{-1} cm^2 mol^{-1} (5.0 × 10^{-4} *M* solution in acetone). Analytical data: % Found· C 34.74, H. 4 04, N: 6.86, Au· 31.40. $C_{18}H_{24}N_3Cl_2O_4Au$ requires: C 35.20, H· 3.94, N: 6.84, Au· 32 06.

cis-*$[Au(o\text{-}O_2NC_6H_4)_2Cl(PPh_3)]$ (III)*

To a suspension of (I) (60 mg, 0.1 mmol) in dichloromethane (20 ml) solid PPh_3 (27 mg, 0.1 mmol) was added. After stirring at room temperature for 5 h the suspension was filtered, the solution concentrated (to 2 ml) and n-hexane added to precipitate (III) (64 mg, 85% yield) as a pale yellow solid. M.p. 151 ℃. Λ_M = 19.5 Ω^{-1} cm^2 mol^{-1} (3.8 × 10^{-4} *M* solution in acetone). Analytical data. % Found. C: 47.92, H. 3.92, N. 3.79, Au. 25.76. $C_{30}H_{23}N_2ClO_4PAu$ requires. C 48 76, H· 3.14, N 3.79, Au· 26.66.

cis-*$[Au(2\text{-}H_3C, 6\text{-}O_2NC_6H_3)_2Cl(PPh_3)]$ (IV)*

To a suspension of (II) (171 mg, 0.28 mmol) in dichloromethane (10 ml) solid PPh_3 (118 mg, 0.45 mmol) was added. After stirring at room temperature for 1 h the suspension was filtered, the solution concentrated (to 2 ml) and diethyl ether added to precipitate (IV) (165 mg, 77% yield) as a pale yellow solid. M p. 165 ℃ (d). Λ_M = 0.7 Ω^{-1} cm^2 mol^{-1} (1.4 × 10^{-4} *M* solution in acetone) Analytical data: % Found: C. 50.22. H: 3.74, N 3 56, Au. 25 17. $C_{32}H_{27}N_2ClO_4PAu$ requires C. 50.11; H: 3.55, N: 3.65, Au. 25.68.

cis-*$[Au(o\text{-}O_2NC_6H_2)_2Cl(py)]$ (V)*

To a suspension of (I) (100 mg, 0.17 mmol) in dichloromethane (25 ml) anhydrous pyridine (0.5 ml) was added and the resulting suspension stirred for 12 h at room temperature and then filtered. The solution was concentrated (to 3 ml) and diethyl ether (25 ml) added to give unreacted (I) and a solution that was concentrated (to 5 ml) and n-hexane added (25 ml) to precipitate (V) (36 mg, 38% yield) as a clear yellow solid. M.p. 120 ℃(d). Λ_M = 15 Ω^{-1} cm^2 mol^{-1} (3.7 × 10^{-4} *M* solution in acetone) Analytical data. % Found C 36 84, H· 3.09, N 7.73, Au 35.01. $C_{17}H_{13}N_3ClO_4Au$ requires C 36.74, H: 2.36, N. 7.56, Au. 35.44

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