C–H Activation of Acetone by 2-Phenylazophenylgold(III) Complexes; Synthesis of the First Acetonylgold(III) Complex

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The complex [Au(2-C_6H_4N=NPh)(CH_2COMe)Cl] (**1**) can be obtained by the reaction of [Au(2-C_6H_4N=NPh)Cl_2] with Tl(acac) (acacH = acetylacetone) in acetone at room temperature, and at 0 °C the intermediate [Au(2-C_6H_4N=NPh)(acac)Cl] (**2**) can be isolated; this and other reactions that lead to complex (**1**), which is the first acetonylgold(III) complex, are the first examples of alkyl C–H activation by a gold(III) complex.

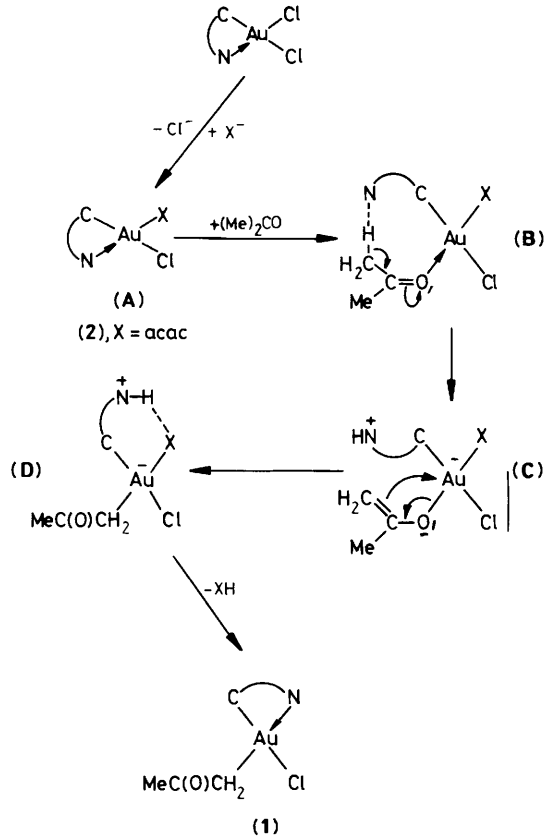
The synthesis of organogold(III) complexes through C–H activation is limited to some arenes which react with $[AuCl_3]_2$ (the so called 'auration' reaction) to give $[Au(aryl)Cl_2]_2$ complexes.[1] There is no report of alkyl C–H activation by a gold(III) complex. Even the auration of arenes has a limited synthetic utility because it is inhibited by the presence of a co-ordinating substituent in the aromatic ring.[2,3] However, we have prepared several examples of orthometallated arylgold(III) complexes by transmetallation reactions using organomercury compounds.[4]

In the development of the chemistry of the orthometallated 2-(phenylazo)phenylgold(III) complexes we have, fortuitously, found that metallation of acetone occurs. Thus, when we tried to prepare [Au(2-C_6H_4N=NPh)(acac)Cl] [acac = $CH\{C(O)Me\}_2$] by the reaction of [Au(2-C_6H_4N=NPh)Cl_2] with Tl(acac) (1 : 1) in acetone (15 min, room temperature) we isolated, instead, the complex [Au(2-C_6H_4N=NPh)(CH_2COMe)Cl] (**1**). Again, when developing our method of synthesis of mixed diarylgold(III) complexes,[4e] we tried to prepare [Au(2-C_6H_4N=NPh)(R)Cl] (R = C_6F_5 or 2-$C_6H_4NO_2$) in acetone,† the only isolable gold complex was (**1**).‡

Although metallation of acetone has previously been described in its reactions with basic oxo- {*e.g.* $[O(AuPPh_3)_3]^+$}[5] or hydroxo-species[6] {*e.g.* [Pt(R)(OH)L_2] (R = Ph, Me; L = PR_3}, the above reactions leading to (**1**) seem to be of a different kind. As far as we know, the sole previous report of a similar behaviour has only recently appeared.[7] Thus, a series of Rh^{III} complexes [RhCl(porphyrin)] react with acetone (at 50 °C or room temperature) to give the corresponding [Rh(CH_2COMe)(porphyrin)] complexes. The presence of a phenolic hydroxyl or quinolyl nitrogen suitably located out of the plane of the porphyrin molecule seems to be essential for the metallation to occur, thus suggesting that the oxygen or nitrogen atoms act as a base to promote enolization of acetone in co-operation with the central Rh^{III}.

Whatever the mechanistic details of the reactions leading to (**1**) might be, it is reasonable to postulate the intermediates shown in Scheme 1. The first step, which gives the intermediate (**A**), is essential because [Au(2-C_6H_4N=NPh)Cl_2] does not react with acetone (93 h at room temperature or refluxing for 3 h). In the case of X = acac we have isolated this intermediate [Au(2-C_6H_4N=NPh)(acac)Cl] (**2**)§ by carrying out the reaction of [Au(2-C_6H_4N=NPh)Cl_2] and Tl(acac) in dichloromethane or in acetone at 0 °C. Complex (**2**) reacts with acetone at room temperature to give (**1**) (15 h, 90% yield). Complex (**1**) does not react with a large excess of acacH (24 h, room temperature) to give (**2**).

As the ligands acac, C_6F_5, and $C_6H_4NO_2$ have a greater *trans* effect and influence than the chloro ligand, it is reasonable to postulate that this is why acetone can be co-ordinated to give (**B**) when X is one of those carbon donor ligands and not when X = Cl. When the same reagents that give (**1**) from [Au(2-C_6H_4N=NPh)Cl_2] react with [Au(2-



Scheme 1. C^N = 2-C_6H_4N=NPh; X = acac, C_6F_5, 2-$C_6H_4NO_2$.

† By the reaction at room temperature of [Au(2-C_6H_4N=NPh)Cl_2] with [R_2Hg] + Cl^- (2 : 1 : 2; 48 h) or with [Pd{2-$C_6H_4N(O)O$}$_2$] (1 : 1; 40 h).

‡ The yellow complex (**1**) gave satisfactory elemental analyses, m.p. 163 °C; Λ_M: 1 Ω^{-1} cm^2 mol^{-1} (2 × 10^{-4} mol dm^{-3} in acetone); ν(CO) 1675 (vs); ν(AuCl) 305 (m) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, tetramethylsilane as reference, 80 MHz): δ 2.38 (s, 3H, CH_3); 3.45 (s, 2H, CH_2); 7.44—7.94 (m, 9H, Ph). The yields depend on the nature of X [X = acac (83%), C_6F_5, or $C_6H_4NO_2$ (50%)].

§ The orange complex (**2**) was obtained by the reaction of [Au(2-C_6H_4N=NPh)Cl_2] with Tl(acac) (1 : 1) in dichloromethane at room temperature (75% yield). It gave satisfactory elemental analyses, m.p. 137 °C; Λ_M: 2 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol dm^{-3} in acetone); ν(CO) 1675, 1690 (vs); ν(AuCl) 308 (m) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, Me_4Si as reference, 80 MHz): 2.37 (s, 6H, CH_3); 4.85 (s, 1H, CH); 7.44—7.82 (m, 9H, Ph).

$C_6H_4CH_2NMe_2)Cl_2]$, the expected complexes $[Au(2\text{-}C_6H_4CH_2NMe_2)(X)Cl]$ are obtained but they do not react with acetone. This observation may be interpreted, in accordance with our proposed pathway, as a consequence of the non-co-ordination of acetone to give an intermediate of type (**B**). We have previously[4] shown that $[Au(2\text{-}C_6H_4N=NPh)Cl_2]$ reacts with neutral ligands to give first the complexes resulting from N ⟶ Au bond cleavage while all attempts to cleave the N ⟶ Au bond in $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ (even with PPh_3) have been unsuccessful.

The enolization process (**B**) ⟶ (**C**) is the result of the co-operation between the acidic metal centre and one of the two basic nitrogen atoms of the azo-group. This step is similar to that proposed to justify the activation of acetone by [RhCl(porphyrin)][7] and also to the enolization processes catalysed by metalloenzymes such as aldolases.[8]

The process is completed when the azonium cation (**D**) transfers the proton to the X ligand to give XH and the chelate is re-established.¶

The proposed geometries of complexes (**1**) and (**2**) are based on the assignment of the ν(AuCl) bands in their i.r. spectra.[4]

¶ According to the above proposed pathway the previously reported[4f] $[Au(2\text{-}C_6H_4N=NPh)(2\text{-}C_6H_4N=NC_6H_5)Cl]$ should also give complex (**1**) in acetone (X = 2-C_6H_4N=NPh in Scheme 1). Actually, although that complex was obtained in dichloromethane by the reaction of $[NMe_4][AuCl_4]$ and $[Hg(2\text{-}C_6H_4N=NPh)_2]$ (1 : 1), when the reaction is carried out in acetone at room temperature (24 h) complex (**1**) is obtained. However, in this case other simultaneous reactions occur leading to metallic gold and the product of the coupling of both phenyl groups. In a refluxing reaction in acetone (3 h) decomposition to metallic gold and formation of $[Au(2\text{-}C_6H_4N=NPh)_2][AuCl_4]$ was observed.

The reactivity of ketones with different 2-C_6H_4N=NPh gold(III) complexes is being studied.

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References

1 M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 1931, **53**, 3053; M. S. Kharasch and T. M. Beck, *ibid.*, 1934, **56**, 2057.
2 P. W. J. de Graaf, J. Boersma, and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1976, **105**, 399.
3 R. Hüttel and A. Konietzny, *Chem. Ber.*, 1973, **106**, 2098; F. Calderazzo and D. Belli Dell'Amico, *J. Organomet. Chem.*, 1974, **76**, C59; P. K. Monaghan and R. J. Puddephatt, *Inorg. Chim. Acta*, 1975, **15**, 231.
4 (a) J. Vicente and M. T. Chicote, *Inorg. Chim. Acta*, 1981, **54**, L259; (b) J. Vicente, M. T. Chicote and M. D. Bermúdez, *ibid.*, 1982, **63**, 35; (c) J. Vicente, M. T. Chicote, M. D. Bermúdez, *J. Organomet. Chem.*, 1984, **268**, 191; (d) J. Vicente, M. T. Chicote, M. D. Bermúdez, and M. García-Garcia, *ibid.*, 1985, **295**, 125; (e) J. Vicente, M. T. Chicote, M. D. Bermudez, M. J. Sanchez-Santano, P. G. Jones, C. Fittschen, and G. M. Sheldrick, *ibid.*, 1986, **310**, 401; (f) J. Vicente, M. T. Chicote, M. D. Bermúdez, X. Solans, and M. Font-Altaba, *J. Chem. Soc., Dalton Trans.*, 1984, 557; (g) J. Vicente, M. T. Chicote, M. D. Bermúdez, P. G. Jones, C. Fittschen, and G. M. Sheldrick, *ibid.*, 1986, 2361; (h) J. Vicente, M. T. Chicote, M. D. Bermúdez, P. G. Jones, and G. M. Sheldrick, *J. Chem. Res.*, 1985, (*S*) 72; (*M*) 0954.
5 H. Schmidbaur, 'Gmelin Handbuch der Anorganischen Chemie, Organogold Compounds,' Springer, Berlin, 1980, p. 25.
6 D. P. Arnold and M. A. Bennet, *J. Organomet. Chem.*, 1980, **199**, 119.
7 Y. Aoyama, A. Yamagishi, Y. Tanaka, H. Toi, and H. Ogoshi, *J. Am. Chem. Soc.*, 1987, **109**, 4735.
8 E. T. Kaiser and T. Sugimoto, *J. Am. Chem. Soc.*, 1978, **100**, 7750.