ature, the solution had changed to bright red and balls of elemental mercury and a white-gray precipitate had formed. TLC indicated the formation of three orange-red products. The solvent was removed in vacuo to yield a red oily solid, which was dissolved in pentane/CH_2Cl_2 (2:1 v/v) and filtered through a thin pad of silicic acid. Removal of the solvent on a rotary evaporator left a dark red oily solid, which was purified by preparative thin-layer chromatography with pentane as the eluent. The first red band gave 0.17 g (0.4 mmol, 15%) of $(\mu\text{-}\sigma,\pi\text{-CH=CHCH}_3)(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ as a slightly air-sensitive red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[1e] The second band was orange-red and gave 0.38 g (0.94 mmol, 61% based on S) of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. The third red band gave 0.23 g (0.57 mmol, 19%) of $(\mu\text{-CH}_3\text{CH=CHC=O})(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6$ (a mixture of two inseparable isomers) as a slightly air-sensitive red oil, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[1e]

X-ray Crystallography. Structure of $(\mu\text{-CH}_3\text{CO}_2)(\mu\text{-}t\text{-BuS})\text{Fe}_2(\text{CO})_6$. Orange crystals of $(\mu\text{-CH}_3\text{CO}_2)(\mu\text{-}t\text{-BuS})\text{Fe}_2(\text{CO})_6$ were grown from pentane at −18 °C over several days. A suitable single crystal was mounted in air on a glass fiber with use of epoxy resin. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $16.0 \leq 2\theta \leq 26.0°$. A triclinic crystal system was established by the usual peak search and reflection indexing program, and the lack of systematic absences established the space group as $P1$ or $P\bar{1}$, the latter of which was established by the satisfactory refinement of the structure. A cell reduction failed to show the presence of a higher symmetry cell.

Intensity data were collected on the CAD4 diffractometer using the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak width on either side of the scan. The intensities of three standard reflections were measured every 60 min of X-ray exposure time; no significant change in these standards occurred, so no correction was applied. The data were processed in the usual manner with a value of 0.04 for p.[22] A total of 5839 unique reflections were measured, of which 3310 were observed and used in subsequent calculations. A summary of data collection details and crystal data appears in Table XIII.

The structure was solved with use of MULTAN 82 to locate the four independent Fe and the two S atoms of the two crystallographically independent complex molecules. All remaining atoms (including hydrogens) were located by the usual sequence of least-squares and difference Fourier calculations.[23] Hydrogen atoms were input in positions idealized from the observed positions, assuming tetrahedral geometries about the carbon atoms and using C–H distances of 0.95 Å. Hydrogens were assigned isotropic thermal parameters 20% larger than those of the attached carbon. All non-hydrogen atoms with the exception of the carbonyl carbon atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[24] An absorption correction was applied to the data by using the method of Walker and Stuart.[25] The final model in the space group $P\bar{1}$ converged to $R = 0.055$ and $R_w = 0.093$ with 325 parameters varied. The asymmetric unit contains two independent $(\mu\text{-CH}_3\text{CO}_2)(\mu\text{-}t\text{-BuS})\text{Fe}_2(\text{CO})_6$ molecules having essentially identical sets of bond distances and angles.

The positional and isotropic thermal parameters for the independent molecules, labeled molecules 1 and 2, are given in Table XIV.

Acknowledgment. The authors at the Massachusetts Institute of Technology are grateful to the National Science Foundation for generous support of this work, while those at the University of Alberta thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Alberta for financial support.

Supplementary Material Available: Tables of infrared and mass spectra for new compounds and anisotropic thermal parameters and hydrogen atom positions for **13a** (19 pages); a listing of the observed and calculated structure factors for **13a** (17 pages). Ordering information is given on any current masthead page.

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[23] Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

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Gold in Organic Synthesis. Preparation of Symmetrical and Unsymmetrical Biaryls via C–C Coupling from *cis*-Diarylgold(III) Complexes

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At room temperature, reacting *cis*-[Au(Ar)(Ar′)Cl] with $[\text{PhCH}_2\text{PPh}_3]\text{Cl}$ (1:1), with PPh_3 plus $\text{NaClO}_4{\cdot}\text{H}_2\text{O}$ (1:2:1), or with PPh_3 (1:1) leads to a reductive elimination giving gold(I) complexes $[\text{PhCH}_2\text{PPh}_3][\text{AuCl}_2]$, $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$, or $[\text{AuCl}(\text{PPh}_3)]$, respectively, and in high yields, the corresponding biaryls Ar–Ar′ [Ar = $\text{C}_6\text{H}_4\text{N=NPh-2}$, Ar′ = Ar (**1**), $\text{C}_6\text{H}_4\text{NO}_2\text{-2}$ (**2**), C_6F_5 (**3**); Ar = Ar′ = $\text{C}_6\text{H}_3(\text{N=NC}_6\text{H}_4\text{Me-4}')\text{-2, Me-5}$ (**4**); Ar = $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2}$, Ar′ = Ph (**5**), $\text{C}_6\text{H}_4\text{N=NPh-2}$ (**6**), $\text{C}_6\text{H}_3(\text{N=NC}_6\text{H}_4\text{Me-4}')\text{-2, Me-5}$ (**7**)].

Introduction

The synthesis of biaryls has a long history from the old Pschorr reaction (1896)[1] to the last report of Caubère (1989).[2] Most of the reported methods require the use of metals or metal complexes. Thus, the Ullmann reaction[3] or some of its modifications use copper or organocopper

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[1] See for example: Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509.

[2] Lourak, M.; Vanderese, R.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4840, 4844.

[3] See for example: Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613; *Synthesis* **1974**, 63. Normant, J. F. *Synthesis* **1972**, 63. Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.

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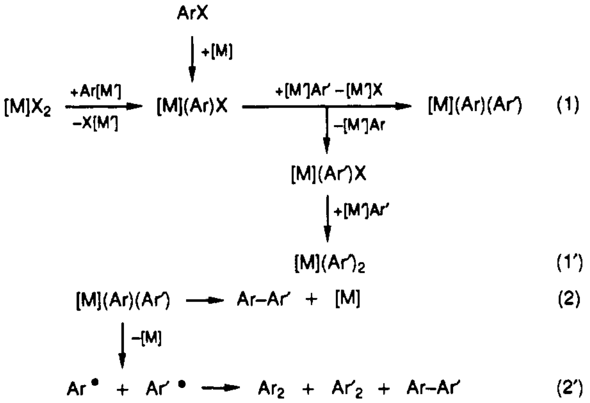
Scheme I. Synthesis of a Biaryl Involving a Diarylmetal Complex Intermediate[a]

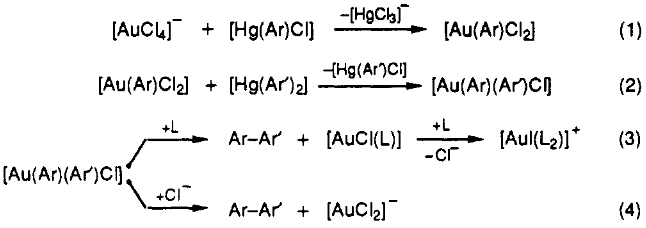


[a] [M] or [M'] represents fragments of two complexes including the metal atom, M or M', and the remaining ligands. M = Ni, Pd, or Pt, and M' = Li, Mg, Zn, Hg, or Sn.

compounds.[4] Nickel,[2,5,6], palladium,[6,7] and other[8] metal complexes have been used in the synthesis of biaryls through stoichiometric or catalytic reactions.

In most cases the diarylmetal complexes, assumed to be intermediates in these reactions,[9] are not isolated. However, some studies have been devoted to their synthesis and isolation and to the study of the C–C coupling process that leads to the biaryls.[10] Pauson[11] reported the synthesis of 1 by reacting $[Rh(C_6H_4N{=}NPh\text{-}2)_2(OAc)]$ (OAc = acetate) with CO, although it was not characterized. Reductive elimination reactions of complexes $[M(Ar)(Ar')L_2]$ (Ar and Ar' = different or equal aryl groups, L = phosphine ligands, M = Ni, Pd, Pt) give biaryls Ar–Ar',[12] but side reactions, when L = Ar''_3P, giving Ar–Ar'' and Ar'–Ar'' are also observed.

Scheme II. Synthesis of Biaryls from Diarylgold(III) Complexes[a]



[a] L = PPh_3. Ar and Ar', see text.

Most of the reported methods for the synthesis of biaryls present restrictions. Thus, the presence of some groups, such as nitro or ortho substituents, on the ring impedes the coupling in most cases. In addition, some methods do not give selectively unsymmetrical biaryls. To circumvent these problems the reductive elimination reactions of diarylmetal complexes (see eqs 1 and 2, respectively, in Scheme I) seem to be very promising.[10–12] However, two main problems must be solved. The first, related to the synthesis of the diaryl complexes, is to design synthetic routes (i) to prepare functionalized aryl complexes (such as those containing nitro groups that usually cannot be easily obtained through the classical ways involving lithium or Grignard reagents), (ii) to prepare mixed diarylmetal complexes (which is not as simple as it is for homodiaryl ones because side reactions can also occur, leading to mixtures of compounds, as shown in eqs 1 and 1' in Scheme I), and (iii) to prepare cis complexes, because such geometry is advisable for the reductive elimination to take place.[10–12] Second, the C–C coupling process should be made in mild conditions otherwise radicals could be formed and mixtures of biaryls could be obtained (eqs 2 and 2').

In this paper we report the use of homo and hetero diarylgold(III) complexes for the synthesis of biaryls. Thermolysis of alkyl- and vinylarylgold(III) species have been shown to give carbon–carbon coupling products.[13] One example of an intramolecular aryl–aryl coupling has been reported for dinuclear gold(II) species,[14] but no reductive biaryl elimination has, to the best of our knowledge, been reported for gold(III) complexes, except preliminary results we have indicated when reporting the properties of some diarylgold(III) complexes.[15]

Results

Addition, at room temperature, to dichloromethane or acetone solutions of *cis*-[Au(Ar)(Ar')Cl], of $[PhCH_2PPh_3]Cl$

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(4) See for example: Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215. Cohnen, T.; Cristea, I. *J. Am. Chem. Soc.* **1976**, *98*, 748. van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Org. Chem.* **1977**, *42*, 2047. Ziegler, F. E.; Chliwner, I.; Fowler, J. N.; Kanfer, S. J.; Kno, S. J.; Sinha, N. D. *J. Am. Chem. Soc.* **1980**, *102*, 790.

(5) See for example: Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908. Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144. Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375. Zembayashi, M.; Tamao, K.; Yoshida, J.-I.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089. Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319, 7547. Semmelhack, M. F.; Helquist, P. M.; Jones, L. D.; Keller, L.; Mendelson, L.; Speltz-Ryono, L.; Gorszynski-Smith, J.; Staufer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460. Matsumoto, H.; Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840. Takagi, K.; Hayama, N.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1887. Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627. Rolling, Y.; Troupel, M.; Tuck, D. G.; Périchon, J. *J. Organomet. Chem.* **1986**, *303*, 131.

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(7) See for example: Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. II, pp 60–71. Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985; pp 180–191. van Helden, R.; Verberg, G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1263. Unger, M. O.; Fouty, R. A. *J. Org. Chem.* **1969**, *34*, 18. Clark, F. R. S.; Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1289. Akermark, B.; Eberson, L.; Jonsson, E.; Pettersson, E. *J. Org. Chem.* **1975**, *40*, 1365. Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253. Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259. Kretchmer, R. A.; Glowive, R. *J. Org. Chem.* **1976**, *41*, 2661. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(8) Larock, R. C.; Bernhardt, J. C. *J. Org. Chem.* **1977**, *42*, 1680.

(9) These intermediates are usually obtained by reacting Li, Mg, Zn, Hg, Sn, etc. aryl compounds with inorganic salts of the transition elements or with the result of reacting a low-valent metal complex with an aryl halide or triflate (see Scheme I).

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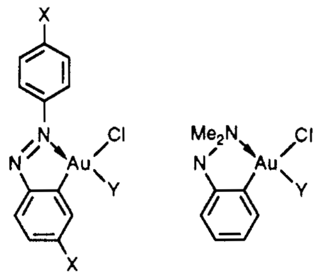
Chart I. Structure of the Arylgold(III) Complexes[a]



[a] $[Au(Ar)Cl_2]$: X = H, Me; Y = Cl. $[Au(Ar)(Ar')Cl]$: X = H, Me; Y = Ar′.

(1:1), PPh_3 plus $NaClO_4{\cdot}H_2O$ (1:2:1), or PPh_3 (1:1) quantitatively yields $[PhCH_2PPh_3][AuCl_2]$, $[Au(PPh_3)_2]ClO_4$, or $[AuCl(PPh_3)]$ respectively, with formation of Ar–Ar′ [Ar = $C_6H_4N{=}NPh$-2, Ar′ = Ar (1), $C_6H_4NO_2$-2 (2), C_6F_5 (3); Ar = Ar′ = $C_6H_3(N{=}NC_6H_4Me$-4′)-2, Me-5 (4); Ar = $C_6H_4CH_2NMe_2$-2, Ar′ = Ph (5), $C_6H_4N{=}NPh$-2 (6), $C_6H_3(N{=}NC_6H_4Me$-4′)-2, Me-5 (7)].

The gold(III) complexes used to prepare the biaryls 1–3, 5, and 6 have already been reported.[15,16] Those giving 4 and 7, containing the aryl group $C_6H_3(N{=}NC_6H_4Me$-4′)-2 and Me-5, can be prepared by following the same method as that used for the synthesis of their homologues containing the $C_6H_4N{=}NPh$-2 group. In general, a monoaryl complex is first prepared by reacting $[AuCl_4]^-$ with the corresponding mercury derivative [Hg(Ar)Cl] (see Scheme II, eq 1). Once the monoaryl complex is isolated, the diaryl complex is obtained via a transmetalation reaction that also uses a mercury compound (eq 2). The reductive elimination process (eq 3 or 4) gives, in high yields, the biaryls and a gold(I) complex. In the case of the reaction with PPh_3, it is frequently more convenient to use an additional 1 mol of the ligand in the presence of $NaClO_4$ to give $[Au(PPh_3)_2]ClO_4$ as the final gold complex, which is better separated from the biaryl due to its insolubility in nonpolar organic solvents.

An important feature of our method is the possibility of recycling gold from the gold(I) byproducts and using it to prepare the starting compounds (see Experimental Section).

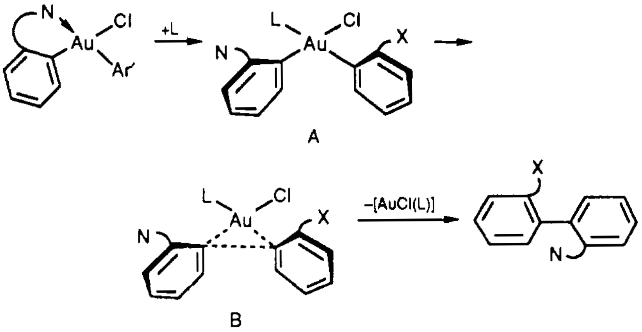
The main purpose of this work was to show, step by step, how some types of biaryls can be prepared from gold(III) complexes. An obvious extension of this work is to find the best conditions to make this synthesis more direct. We have succeeded in the "one-pot synthesis" of 6 (in 55% yield) by reacting the commercially available $Na[AuCl_4]{\cdot}2H_2O$ with Me_4NCl, then $[Hg(C_6H_4CH_2NMe_2\text{-}2)_2]$, and finally, $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$ (2:10:1:1), recuperating gold in the form of $Me_4N[AuCl_4]$ (60% yield).

To the best of our knowledge, this is the first application of organogold(III) complexes in organic synthesis.

Discussion

The monoarylgold(III) complexes $[Au(Ar)Cl_2]$ have in common that the aryl group is acting as a chelating ligand bonded through a carbon and a nitrogen atom, giving a five-membered ring, which allows the gold atom to reach its usual square-planar coordination (see Chart I). The diarylgold(III) complexes [Au(Ar)(Ar′)Cl] have the same chelating Ar ligand, the Ar′ being bonded as monocoordinated and cis to the carbon atom, as have been proved by IR spectroscopy and the crystal structure of those with Ar = $C_6H_4CH_2NMe_2$-2, Ar′ = Ph[15c] and C_6F_5[16,17] as well as those of some of their derivatives (e.g. $[Au(Ar)(Ar')]^+$ with Ar = $C_6H_4N{=}NPh$-2 and Ar′ = Ar[15a] or $C_6H_4CH_2NMe_2$-2[15b]).

Scheme III. Proposed Pathway to the Synthesis of Biaryls from Diarylgold(III) Complexes[a]



[a] PhN and PhX represent Ar and Ar′, respectively.

We postulate that the stability of these diarylgold(III) complexes is due to the chelating nature of the Ar ligand. Other isolated diarylgold(III) complexes, not containing chelating aryl groups, are polyhaloaryl- or *o*-nitroaryl complexes. No diphenylgold(III) complex has yet been reported.[18] The addition of a neutral (PPh_3) or anionic (Cl^-) ligand should cleave the Au–N bond,[16] thus allowing both aryl rings to be positioned perpendicular to the coordination plane. Finally, the coupling could occur through an intermediate (B) formed by a closed three-center four-electron bonding of both carbons and the gold atom (see Scheme III), such as suggested by Cross et al.[12]

In favor of this pathway is the fact that when Ar is $C_6H_4CH_2NMe_2$-2 and Ar′ = Ar, $C_6H_4NO_2$-2, or C_6F_5, the C–C coupling does not occur, while with Ar = $C_6H_4N{=}NPh$-2 the biaryls 6, 2, and 3 are easily obtained because of the much weaker N→Au bond in the $C_6H_4N{=}NPh$-2 than in the $C_6H_4CH_2NMe_2$-2 derivatives.[15,16] In addition, the synthesis of 5 in spite of the presence of the strong chelating $C_6H_4CH_2NMe_2$-2 group suggests that the coupling also depends on the strength of the Ar′–Au bond, which, as mentioned above, is particularly weak in the case of Ar′ = Ph. This is reasonable, according to the proposed pathway, because the conversion of intermediate A into the biaryl plus the gold(I) complex requires the cleavage of the C···Au bonds.

The thermal decomposition of trialkyl- or dimethylaryl(triarylphosphine)gold(III) complexes proceeds via dissociation of the phosphine ligand.[13] Addition of phosphine strongly suppress the rate of the thermolysis, which contrasts with our C–C coupling process, suggesting a different mechanism.

In all cases ^1H and ^{13}C NMR data (see Tables I and II) are in accordance with the formation of only the isomer resulting from the C–C coupling. ^{13}C NMR data agree with theoretical values calculated by assuming additive effects for the different substituents.[20] The only misfitting refers to the resonances found at around 115 ppm in all biaryls containing a 2-(phenylazo)phenyl group: that we have assigned to the CH carbon atom ortho to the azo group. The difference between the calculated and observed values

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Table I. ^1H **NMR Data**[a,b]

biaryl	
1	7.16–7.36 (m, 6 H, H_4–H_6), 7.39–7.64 (m, 10 H, H_8–H_{10}), 7.70–7.81 (m, 2 H, H_3)
2	7.32–7.61 (m, 11 H, H_4–H_6, $H_{4'}$–$H_{6'}$, H_8–H_{10}), 7.70 (m, 1 H, H_3), 7.95–7.99 (m, 1 H, $H_{3'}$)
3	7.37–7.51 (m, 3 H, H_4–H_6), 7.57–7.71 (m, 5 H, H_8–H_{10}), 7.88–7.91 (m, 1 H, H_3)
4	2.30 (s, 6 H, *Me*–Ph), 2.48 (s, 6 H, *Me*–Ph), 7.07, 7.36 (AB, H_8, H_9, J_{HH} = 8 Hz), 7.31–7.40 (m, 2 H, H_4, H_6), 7.69 (d, 1 H, H_3, J_{34} = 8 Hz)
5	2.14 (s, 6 H, N*Me*$_2$), 3.34 (s, 2 H, CH_2), 7.20–7.40 (m, 8 H, H_4–H_6, $H_{2'}$–$H_{6'}$), 7.53–7.57 (m, 1 H, H_3)
6	2.02 (s, 6 H, N*Me*$_2$), 3.20, 3.22 (AB, CH_2, J_{HH} = 14 Hz), 7.23–7.62 (m, 11 H, H_4–H_6, $H_{4'}$–$H_{6'}$, H_8–H_{10}), 7.73–7.77 (m, 2 H, H_3, $H_{3'}$)
7	2.02 (s, 6 H, N*Me*$_2$), 2.34 (s, 3 H, *Me*–Ph), 2.44 (s, 3 H, *Me*–Ph), 3.19, 3.22 (AB, CH_2, J_{HH} = 14 Hz), 7.15, 7.46 (AB, H_8, H_9, J_{HH} = 8 Hz), 7.13–7.56 (m, 6 H, H_4, H_6, $H_{3'}$–$H_{6'}$), 7.67 (d, 1 H, H_3, J_{34} = 8 Hz)

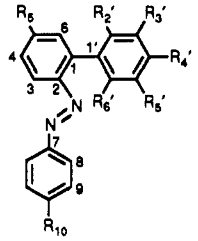
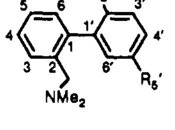
[a] δ (ppm, TMS), 200 MHz, $CDCl_3$. [b] See Table III for atom numbering.

Table II. ^{13}C **NMR Data**[a,b]

	1	2	3[c]	4	5	6	7
C_1	138.9 (135.8)	134.4 (135.8)		140.1 (135.7)	142.4 (142.3)	131.4 (135.8)	136.2 (135.7)
C_2	150.7 (151.4)	148.8 (151.4)	149.7	148.9 (148.5)	136.4 (139.9)	150.2 (151.4)	148.0 (148.5)
C_3	115.2[c] (123.5)	115.7[c] (123.5)	116.2	114.8[c] (123.4)	126.6 (127.0)	115.3[c] (123.5)	115.0[c] (123.4)
C_4	130.5 (130.7)	131.2 (130.7)	131.3	129.2 (128.4)	127.2 (127.3)	130.4 (130.7)	124.4 (124.2)
C_5	131.8 (131.1)	131.3 (131.1)	131.5	140.5 (140.0)	126.7 (127.2)	131.3 (131.1)	140.9 (140.0)
C_6	128.4 (127.7)	128.4 (127.7)	130.8	129.0 (128.3)	129.7 (127.4)	127.7 (127.7)	128.5 (128.4)
$C_{1'}$	138.9 (135.8)	138.3 (135.8)		140.1 (135.7)	141.5 (141.5)	141.3 (142.3)	141.0 (142.3)
$C_{2'}$	150.7 (151.4)	148.8 (151.4)		148.9 (148.5)	127.8 (127.4)	139.3 (139.9)	139.5 (139.9)
$C_{3'}$	115.2[c] (123.5)	123.9 (124.1)		114.8[c] (123.4)	129.5 (128.0)	127.3 (127.4)	127.6 (127.4)
$C_{4'}$	130.5 (130.7)	128.3 (128.2)		129.2 (128.4)	129.9 (129.5)	127.6 (127.3)	127.5 (127.3)
$C_{5'}$	131.8 (131.1)	132.8 (134.7)		140.5 (140.0)	129.5 (128.0)	127.0 (127.0)	127.4 (127.0)
$C_{6'}$	128.4 (127.7)	128.6 (128.3)		129.0 (128.3)	127.8 (127.4)	127.4 (127.2)	126.1 (127.2)
C_7	152.6 (152.5)	152.5 (152.5)	152.4	150.9 (149.4)		152.7 (152.5)	150.8 (149.4)
C_8	122.9 (123.1)	123.2 (123.1)	122.8	122.7 (122.7)		123.0 (123.1)	122.7 (122.7)
C_9	128.7 (128.8)	128.9 (128.8)	129.0	129.5 (129.4)		129.0 (128.8)	128.8 (129.4)
C_{10}	130.0 (130.0)	129.8 (130.0)	130.3	139.0 (140.0)		130.0 (130.0)	140.6 (140.0)
CH_2					60.9	61.2	60.8
Me$_2$N					45.2	45.4	45.0
Me–Ph				21.3 21.4			21.3 21.4

[a] δ (ppm, TMS), 50.32 MHz, $CDCl_3$. Calculated values are given in parenthesis. [b] See Table III for atom numbering. [c] See text.

Table III. Atom Numbering[a] **and Isolated Yields**[b]

compd		isolated yield
		
1	$R_5 = R_{10} = H$; $R_{2'} = N_2Ph$	90
2	$R_5 = R_{10} = H$; $R_{2'} = NO_2$	68
3	$R_5 = R_{10} = H$; $R_{2'} = R_{3'} = R_{4'} = R_{5'} = R_{6'} = F$	80
4	$R_5 = R_{10} = Me$; $R_{2'} = N_2C_6H_4Me\text{-}4$	85
		
5	$R_{2'} = R_{5'} = H$	73[c]
6	$R_{2'} = N_2Ph$	63
7	$R_{2'} = N_2C_6H_4Me\text{-}4$; $R_{5'} = Me$	80

[a] The atom numbering is that used for Tables I and II. C and H numbering is the same as that of the R group attached to it or that takes its place, respectively. [b] Isolated yields (%) are for conversion of cyclometalated gold(III) complexes to biaryls. [c] Compound 5 can be formed in one pot from Na[$AuCl_4$] in 55% isolated yield.

(see Table II) might be due to some interaction with the nitrogen atoms of the azo groups.

The steric requirement of some substituents inhibit the free rotation around the C_1–$C_{1'}$ bond, giving rise to the well-known torsional atropisomerism. This restricted rotation causes the –CH_2– group to appear as an AB system in the ^1H NMR spectra of compounds 6 and 7. ^{19}F–^{13}C couplings are responsible for the lack of observation of the ^{13}C resonances of the C_6F_5 group in compound 3; ^{19}F NMR spectra show the typical signals for the presence of a pentafluorophenyl ring. Mass spectra show the molecular ion in all cases (see Experimental Section). IR spectra show bands assignable to the different types of substitution on the phenyl rings and some characteristic absorptions of functional groups such as *o*-NO_2 or C_6F_5 (see Experimental Section).

Conclusions

The reactions of diarylgold(III) complexes with some ligands (PPh_3 or Cl^-) allow the high yield and very mild synthesis of homo and hetero biaryls. The synthesis is possible even if both aryl groups contain ortho substituents or if one of them is an *o*-nitrophenyl group, and it is facilitated by the tendency of gold(III) complexes to give cis complexes. Because the ability of a diarylmetal complex to give a biaryl depends on its stability, our data suggest that gold complexes should be superior than those of palladium(II) or platinum(II) and similar to those of nickel(II). However, more experimental data are required to know the limits of this rule.

Experimental Section

C, H, and N analyses, melting point determinations, and recording of the IR and NMR spectra were performed as described elsewhere.[19] Reactions were carried out at room temperature with magnetic stirring without special precautions to exclude light or moisture. The recipes below are for the best yield method. The relevant ^1H and ^{13}C NMR spectroscopic data and isolated yields are included in Tables I–III, respectively. ^{19}F NMR data are given below. Gold complexes were obtained as reported.[15,16]

Synthesis of Biaryls 1 and 4. To a CH_2Cl_2 solution (150 mL) of the corresponding diarylgold(III) complex (1.2 mmol) was added solid $[PhCH_2PPh_3]Cl$ (1.2 mmol). After 48 h of stirring, solvent was removed under vaccum and the residue extracted with *n*-hexane (5 × 10 mL). Filtration gave a white solid, $[PhCH_2PPh_3][AuCl_2]$, and a red solution, which after filtration was concentrated (to ca. 2 mL) and chromatographied through silica gel (3 × 20 cm). Elution with CH_2Cl_2/*n*-hexane (1:20) gave an orange-red band. The solution was evaporated to dryness to obtain 1 as a red solid: mp 85 °C; MS (*m*/*e*) 362 (M^+, 2%), 257 ($C_{18}H_{13}N_2$, 100%), 181 ($C_6H_4N_2Ph$, 20%), 152 ($C_{12}H_8$, 19%), 77 (Ph, 59%), 51 (C_4H_3, 27.5%). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.6; H, 5.0; N, 16.5. Found: C, 79.2; H, 5.4; N, 16.7. IR (cm^{-1}): 782 (s, ortho disubstituted), 687 (s, monosubstituted). 4: mp 126 °C; MS (*m*/*e*) 418 (M^+, 3%), 91 ($CH_3C_6H_4$ and HNC_6H_4, 100%). Anal. Calcd for $C_{28}H_{26}N_4$: C, 80.4; H, 6.3; N, 13.4. Found: C, 79.7; H, 5.8; N, 12.9. IR (cm^{-1}): 830 (m, trisubstituted), 770 (s, para disubstituted).

Synthesis of Biaryls 2, 3, 6, and 7. To an acetone solution (30 mL) of the corresponding diarylgold(III) complex (0.9 mmol) were added solid PPh_3 (1.8 mmol) and $NaClO_4{\cdot}H_2O$ (0.9 mmol), and the mixture was stirred for 48 h. The solution was then evaporated to dryness and the residue extracted with *n*-hexane (5 × 10 mL) to separate a white solid ($[Au(PPh_3)_2]ClO_4$ + NaCl) and a red solution, which after filtration was evaporated to dryness. Workup as above gave orange-red microcrystals of the biaryls. 2: mp 85 °C; MS (*m*/*e*) 303 (M^+, 1%), 139 ($C_6H_7N_2O_2$, 32%), 115 (C_9H_7, 28%), 77 (Ph, 100%), 51 (C_4H_3, 34%). Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.3; H, 4.3; N, 13.8. Found: C, 71.9; H, 4.6; N, 13.2. IR (cm^{-1}): 1520 (s, ν_{asym} NO_2), 1350 (s, ν_{sym} NO_2), 850 (m, ν ONO), 773 (s, ortho disubstituted), 687 (s, monosubstituted). 3: mp 94 °C; MS (*m*/*e*) 348 (M^+, 3%), 243 ($M^+ - C_{12}H_4F_5$, 7.2), 105 (N_2Ph, 17%), 77 (Ph, 100%), 51 (C_4H_3, 34%). Anal. Calcd for $C_{18}H_9N_2F_5$: C, 62.1; H, 2.6; N, 8.0. Found: C, 62.8; H, 3.0; N, 8.5. ^{19}F NMR: −140.2 (m, *o*-F), −155.5 (t, J_{FF} = 21 Hz, *p*-F), 163.4 (m, *m*-F) ppm (referred to $CFCl_3$). IR (cm^{-1}): 1500 (s), 1060 (s), 860 (s, C_6F_5), 775 (s, ortho disubstituted), 687 (s, monosubstituted). 6: mp 82 °C; MS (*m*/*e*) 315 (M^+, 3%), 180 ($C_{12}H_8N_2$, 100%), 165 ($C_{13}H_9$, 51%). Anal. Calcd for $C_{21}H_{21}N_3$: C, 80.0; H, 6.7; N, 13.3. Found: C, 81.2; H, 7.3; N, 14.4. IR (cm^{-1}): 770 (s), 742 (s ortho disubstituted), 687 (s, monosubstituted). 7: mp 60 °C; MS (*m*/*e*) 343 (M^+, 6%), 194 ($C_{13}H_{10}N_2$, 100%), 299 ($M^+ - NMe_2$, 36.3%). Anal. Calcd for $C_{23}H_{25}N_3$: C, 80.4; H, 7.3; N, 12.2. Found: C, 79.1; H, 7.8; N, 13.0. IR (cm^{-1}) 830 (m, trisubstituted), 760 (s, para disubstituted), 742 (ortho disubstituted).

One-Pot Synthesis of 6. To an acetone (50 mL) solution of $Na[AuCl_4]$ (0.5 mmol) were added solid Me_4NCl (1.0 mmol) and $[Hg(C_6H_4CH_2NMe_2\text{-}2)_2]$ (0.25 mmol). After decoloration of the resulting suspension (ca. 30 min), solid $[Hg(C_6H_4N{=}NPh\text{-}2)_2]$ (0.25 mmol) and Me_4NCl (4.0 mmol) were added and the suspension was stirred for 48 h. Removal of the solvent, extraction with *n*-hexane (5 × 10 mL), filtration, and evaporation to dryness afforded 6. The white residue resulting from the *n*-hexane extraction was treated with excess chlorine (CCl_4 solution) and extracted with dichloromethane (10 × 10 mL) to recover $Me_4N[AuCl_4]$ (60% yield).

Synthesis of 5. To a dichloromethane solution (60 mL) of $[Au(C_6H_4CH_2NMe_2\text{-}2)(C_6H_5)Cl]$ (2.7 mmol) was added solid PPh_3 (2.7 mmol). After 16 h of stirring, the solvent was removed and the residue extracted with *n*-hexane (5 × 5 mL). Filtration gave a white precipitate ($[AuCl(PPh_3)]$, 1200 mg) and a colorless solution that was concentrated to dryness to obtain white microcrystals of 5: mp 110 °C; MS (*m*/*e*) 211 (M^+, 14%), 167 ($C_{13}H_{11}$, 100%), 152 ($C_{12}H_8$, 45%), 58 (CH_2NMe_2, 98%). Anal. Calcd for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6. Found: C, 84.1; H, 7.8; N, 7.0. IR (cm^{-1}): 750 (s, ortho disubstituted), 700 (s, monosubstituted).

Gold Recycling. When the gold(I) byproduct is $[PhCH_2PPh_3][AuCl_2]$, method a was followed. If the gold(I) species contain PPh_3 ($[AuCl(PPh_3)]$ or $[Au(PPh_3)_2]ClO_4$) method b gave better yields.

Method a. $[PhCH_2PPh_3][AuCl_2]$ (530 mg) was dissolved in aqua regia (50 mL) and the solution heated (90 °C) to dryness. Concentrated HCl solution (25 mL) was then added and the concentration to dryness repeated. This last treatment was repeated two more times to assure that all nitric acid had been removed. The orange-red residue of $H[AuCl_4]$ was dissolved in ethanol/water (30 mL, 1:1) and solid $[Me_4N]Cl$ (100 mg) added to precipitate $Me_4N[AuCl_4]$ as a yellow solid, which was filtered and washed with water, ethanol, and diethyl ether. Yield: 75%. $Me_4N[AuCl_4]$ is the starting material to prepare $[Au(Ar)_2Cl]$ (Ar = $C_6H_3(N{=}NC_6H_4X\text{-}4')\text{-}2$, X-5; X = H, Me). If $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) is the desired starting material (to prepare $[Au(Ar)Cl_2]$; Ar = $C_6H_4N{=}NPh\text{-}2$ or $C_6H_4CH_2NMe_2\text{-}2$), the ethanol/water solution of $H[AuCl_4]$ must be reduced by dropwise addition of tht just to get a colorless solution and a white solid, $[AuCl(tht)]$. Adding an excess of a carbon tetrachloride solution of chlorine to a dichloromethane solution of this gold(I) complex precipitates most of the $[AuCl_3(tht)]$ formed. Addition of diethyl ether to the resulting mother liquors allows one to isolate the remaining gold(III) complex.

Method b. $[AuCl(PPh_3)]$ or $[Au(PPh_3)_2]ClO_4$ (500 mg) was treated with excess $H_2N\text{-}NH_2{\cdot}H_2O$ and calcinated until a metallic gold residue was obtained. The residue was dissolved in aqua regia (25 mL). Treatment as above yielded $[AuCl_3(tht)]$. Yield: 70–75%.

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