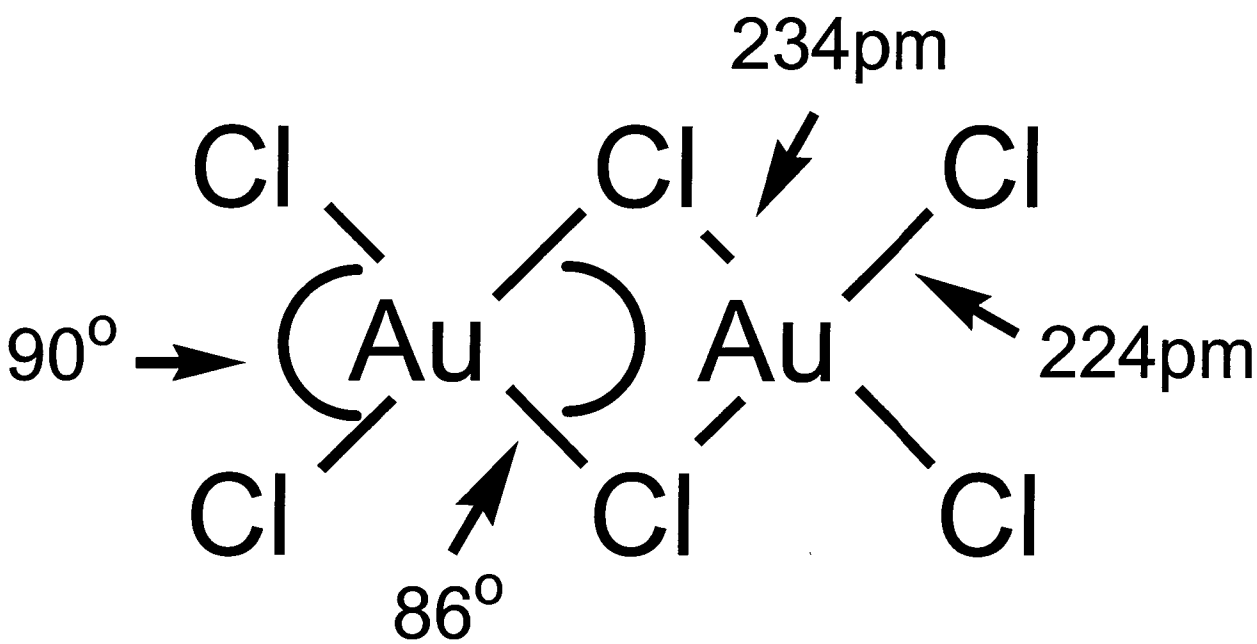
Gold-Catalyzed Reactions

Michael H. Ober

01/30/01

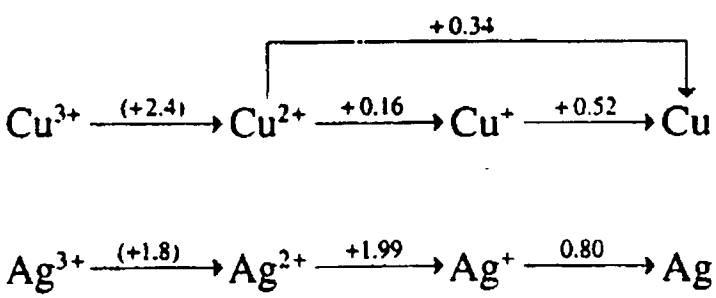
$AuCl_3$ @ 73 g

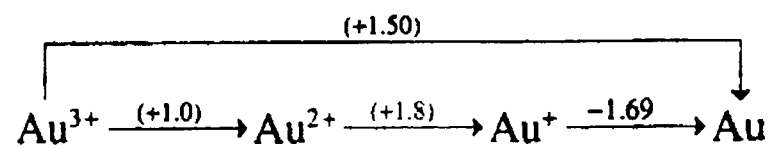


Basics of Gold

Table 28.1 Some properties of the elements copper, silver and gold

Property		Cu	Ag	Au
Atomic number		29	47	79
Number of naturally occurring isotopes		2	2	1
Atomic weight		63.546(3)	107.8682(2)	196.96655(2
Electronic configuration		$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$	$[Xe]4f^{14}5d^{10}6s^1$
Electronegativity		1.9	1.9	2.4
Metal radius (12-coordinate)/pm		128	144	144
Effective ionic radius (6-coordinate)/pm	V	—	—	57
	III	54	75	85
	II	73	94	—
	I	77	115	137
Ionization energy/kJ mol^{-1}	1st	745.3	730.8	889.9
	2nd	1957.3	2072.6	1973.3
	3rd	3577.6	3359.4	(2895)
MP/°C		1083	961	1064
BP/°C		2570	2155	2808
ΔH_{fus}/kJ mol^{-1}		13.0	11.1	12.8
ΔH_{vap}/kJ mol^{-1}		307(±6)	258(±6)	343(±11)
$\Delta H_{(monatomic\ gas)}$/kJ mol^{-1}		337(±6)	284(±4)	379(±8)
Density (20°C)/g cm^{-3}		8.95	10.49	19.32
Electrical resistivity (20°C)/μohm cm		1.673	1.59	2.35





Greenwood, N.; Earnshaw "Chemistry of the Elements" 2nd Ed. **1997**

Gold Related Metals

Table 27.1 Some properties of the elements nickel, palladium and platinum

Property		Ni	Pd	Pt
Atomic number		28	46	78
Number of naturally occurring isotopes		5	6	6[a]
Atomic weight		58.6934(2)	106.42(1)	195.078(2)
Electronic configuration		$[Ar]3d^8 4s^2$	$[Kr]4d^{10}$	$[Xe]4f^{14}5d^9 6s^1$
Electronegativity		1.8	2.2	2.2
Metal radius (12-coordinate)/pm		124	137	138.5
Effective ionic radius (6-coordinate)/pm	V	—	—	57
	IV	48	61.5	62.5
	III	56 (ls), 60 (hs)	76	—
	II	69	86	80
MP/°C		1455	1552	1769
BP/°C		2920	2940	4170
H_{fus}/kJ mol^{-1}		17.2(±0.3)	17.6(±2.1)	19.7(±2.1)
H_{vap}/kJ mol^{-1}		375(±17)	362(±11)	469(±25)
H_f (monatomic gas)/kJ mol^{-1}		429(±13)	377(±3)	545(±21)
Density (20°C)/g cm^{-3}		8.908	11.99	21.45
Electrical resistivity (20°C)/μohm cm		6.84	9.93	9.85

All have zero nuclear spin except ^{195}Pt (33.8% abundance) which has a nuclear spin quantum number $\frac{1}{2}$: this isotope finds wide use in nmr spectroscopy both via direct observation of the ^{195}Pt resonance and even more by the observation of ^{195}Pt "satellites". Thus, a given nucleus coupled to ^{195}Pt will be split into a doublet symmetrically placed about the central unsplit resonance arising from those species containing any of the other 5 isotopes of Pt. The relative intensity of the three resonances will be $(\frac{1}{2} \times 33.8):66.2:(\frac{1}{2} \times 33.8)$, i.e. 1:4:1.

Greenwood, N.; Earnshaw "Chemistry of the Elements" 2nd Ed. **1997**

Gold Structures

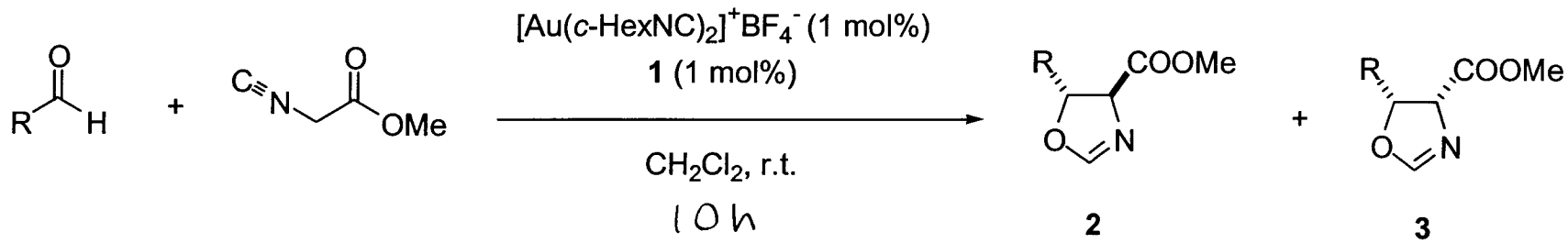
Table 18-I-1 Oxidation States and Stereochemistry of Silver and Gold

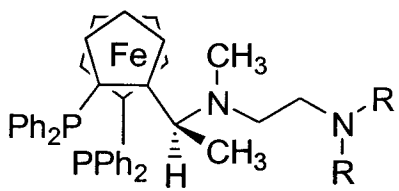
Oxidation state	Coordination number	Geometry	Examples
Ag^{I}, d^{10}	2[a]	Linear	$[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$, AgSCN
	3	Trigonal	$[Ag(PCy_2Ph)_3]BF_4$, $[Au(PCyPh_2)_3]CO_4$
	4[a]	Tetrahedral	$[Ag(SCN)_4]^{3-}$, $[AgI(PR_3)]_4$, $[Ag(py)_4]^+$, $[Ag(PPh_3)_4]ClO_4$
	5	Distorted pentagonal plane	$[Ag(L)]^{+}$ [b]
	5	Pentagonal pyramidal	$[Ag(L)]_2^{2+}$ [b]
	6	Octahedral	AgF, AgCl, AgBr (NaCl structure), $[Ag(18S6)]CF_3SO_3$ [c]
Ag^{II}, d^9	4	Planar	$[Ag(py)_4]^{2+}$
	6	Distorted octahedral	Ag(2,6-pyridinedicarboxylate)$_2 \cdot H_2O$
Ag^{III}, d^8	4	Planar	AgF_4^-, half Ag atoms in AgO, $[Ag(ebbg)_2]^{3+}$ [d]
	6	Octahedral	$[Ag(IO_6)_2]^{7-}$, Cs_2KAgF_6
Au^{I}, d^{10}	2[a]	Linear	$[Au(CN)_2]^-$, $Et_3PAuC{\equiv}CPh$; $(AuI)_n$
	3	Trigonal	$AuCl(PPh_3)_2$
	4	Tetrahedral	$[Au(diars)_2]^+$
Au^{II}, d^9	4	Square	$[Au(mnt)_2]^{2-}$
Au^{III}, d^8	4[a]	Planar	$AuBr_4^-$, Au_2Cl_6, $[(C_2H_5)_2AuBr]_2$, R_3PAuX_3, $[AuPh_4]^-$
	5	*tbp*	$[Au(diars)_2I]^{2+}$
		sp	$AuCl_3$(2,9-Me_2-1,10-phen), AuCl(TPP)
	6	Octahedral	$AuBr_6^{3-}$, *trans*-$[Au(diars)_2I_2]^+$
Au^{V}, d^6	6	Octahedral	$[Xe_2F_{11}]^+[AuF_6]^-$, $[AuF_5]_{2,3}$ (g)

[a]Most common states.
[b]L is an N_5 macrocycle:

Cotton, F.A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. "Advanced Inorganic Chemistry" 6th Ed. **1999**

Gold-Catalyzed Aldol Reactions



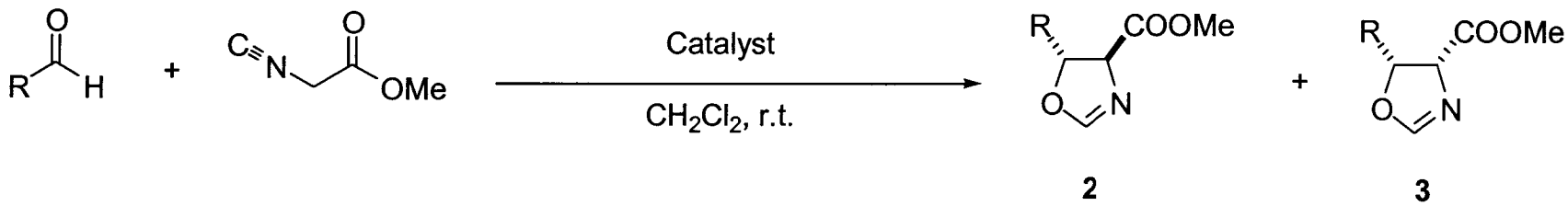


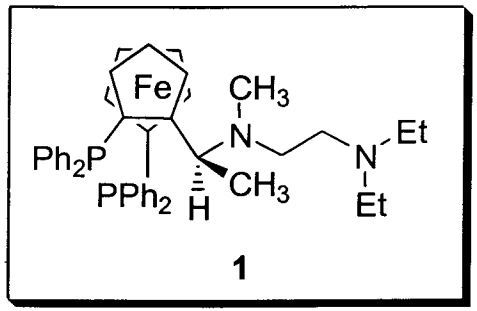
1a NR_2 = NEt_2
1b NR_2 = NMe_2

Entry	Ligand	R	Yield	Ratio (**2** / **3**)	ee% (**2** , **3**)
1	**1a**	Ph	98	98 / 11	96% , 49%
2	**1b**	Ph	91	80 / 10	94% , 4%
3	**1a**	*n*-PrCH=CH	83	81 / 19	84% , 52%
4	**1b**	*n*-PrCH=CH	97	80 / 20	87% , 0%
5	**1a**	Me	100	84 / 16	72% , 44%
6	**1a**	*i*-Pr	99	98 /2	92%
7	**1a**	*c*-Hex	95	97 / 3	90%
8	**1b**	*c*-Hex	96	98 / 2	81%
9	**1a**	*t*-Bu	100	100 / 0	97%

Ito, Y.; Sawamura, M.; Hayashi, T. *J. Org. Chem.*. **1986**, *108*, 6405

Gold-Catalyzed Aldol Reactions





Entry	Catalyst	R	Yield	Ratio (**2** / **3**)	ee% (**2**)
1	**A**	Ph	98	89 / 11	96%
2	**B**	Ph	90	96 / 4	80%
3	**A**	*i*-Pr	99	98 / 2	92%
4	**B**	*i*-Pr	90	98 / 2	90%
5	**A**	*t*-Bu	100	100 / 0	97%
6	**B**	*t*-Bu	91	99 / 1	88%

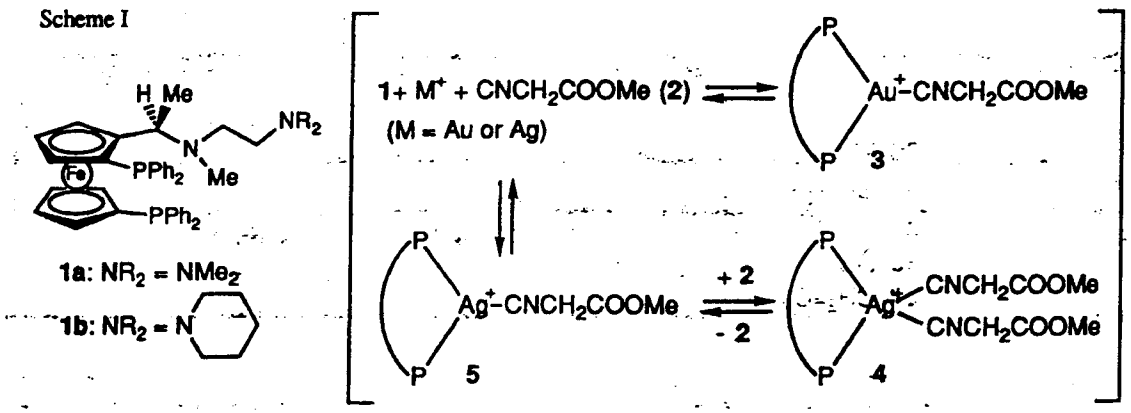
Catalyst A : $[Au(c\text{-}HexNC)_2]^+BF_4^-$ (1 mol%), **1** (1 mol%)

Catalyst B : $AgClO_4$ (2 mol%), **1** (2 mol%)

Hayashi, T.; Uozumi, Y.; Yamazaki, A. *Tetrahedron Lett.*. **1991**, *32*, 2799

Gold-Catalyzed Aldol Reactions

Scheme I



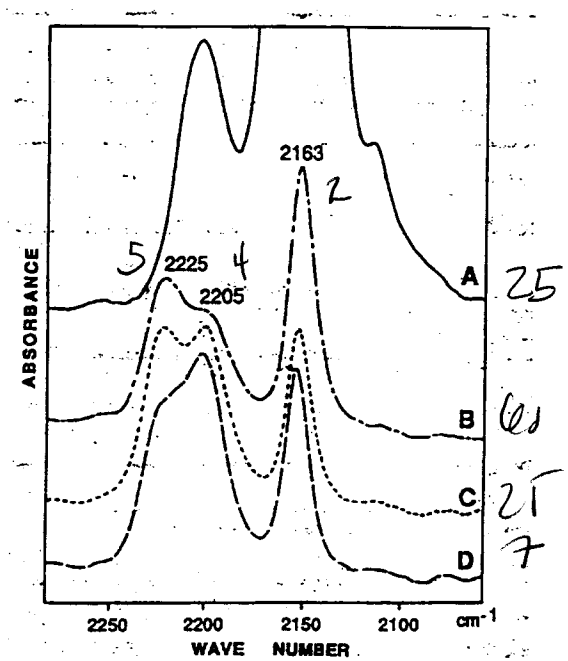
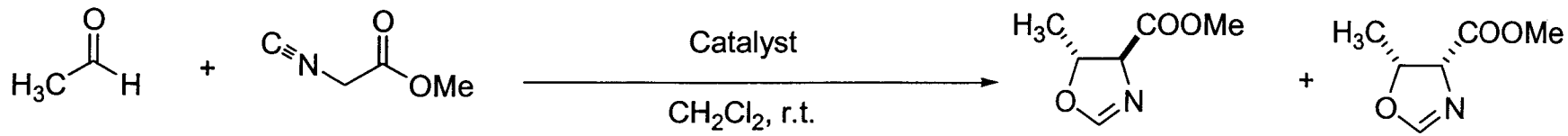


Figure 1. FTIR spectra of a mixture of $CNCH_2COOMe$ (2), AgOTf, and ferrocenylbisphosphine 1a in 1,2-dichloroethane. A: 2/AgOTf/1a = 20/1/1 (6.25 mM) at 25 °C. B-D: 2/AgOTf/1a = 1/1/1 (12.5 mM), at 60 °C (B), at 25 °C (C), and at 7 °C (D). The peaks at 2163, 2205, and 2225 cm^{-1} are assigned to CN stretchings of 2, 4, and 5, respectively.

Hayashi, T.; Uozumi, Y.; Yamazaki, A. *Tetrahedron Lett.*. **1991**, *32*, 2799

Gold-Catalyzed Aldol Reactions



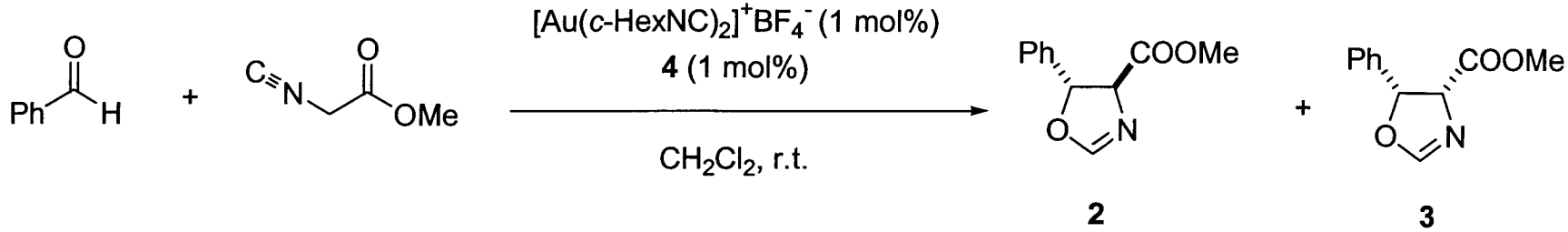
1. Asymmetric Aldol Rection of Methyl Isocyanoacetate with Acetaldehyde (6a)[a]

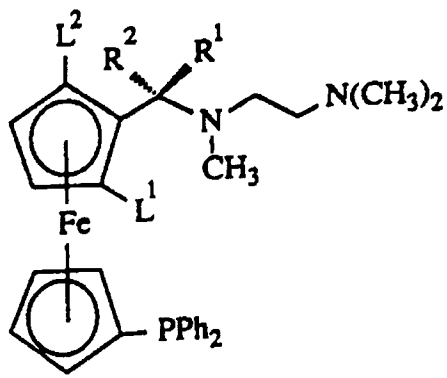
ligand 1 side chain	yield[b] % of 7a	ratio[c] of *trans/cis*	% ee[d] *trans*-(4*S*,5*R*)-7a	% ee[d] (config *cis*-7a
NMe, NMe_2	94	78/22	37	0
NMe, NEt_2	100	84/16	72[e]	44 (4*R*,5*R*)
NMe, N(*n*-Bu)$_2$	100	78/22	71	40 (4*R*,5*R*)
NMe, N(*n*-Oct)$_2$	96	74/26	45	27 (4*R*,5*R*)
NMe, N(*i*-Pr)$_2$	99	70/30	55	68 (4*R*,5*R*)
NMe, N	83	87/13	74	18 (4*R*,5*R*)
NMe, N	100	85/15	85	56 (4*R*,5*R*)
NMe, N	100	83/17	78	32 (4*R*,5*R*)
NMe, N, O	99	89/11	89	10 (4*S*,5*S*)
NMe, N, S	100	88/12	85	18 (4*R*,5*R*)
NMe, N, NMe	85	89/11	83	50 (4*R*,5*R*)
NMe, N	100	79/21	86	70 (4*R*,5*R*)
NMe, N	100	85/15	82	43 (4*R*,5*R*)
NMe, N	100	86/14	84	47 (4*R*,5*R*)
NMe, N	100	84/16	86	61 (4*R*,5*R*)
NMe, N	94	76/24	58	7 (4*S*,5*S*)
NMe, N	100	77/23	42	2 (4*S*,5*S*)
N, H, N, O	67	77/23	28	6 (4*R*,5*R*)
N, Bu-*i*, N, O	98	84/16	79	12 (4*R*,5*R*)

he reaction was carried out in dichloromethane at 25 °C for 10-20 h. Isocyanoacetate/6a/Au/1 0.010/0.011 unless otherwise noted. [b] Isolated yield by bulb-to-bulb distillation. [c] Determin NMR analysis. [d] Determined by ^{1}H NMR spectra using chiral shift reagent Eu(dcm)$_3$. [e] $[\alpha]_D$ 3° (THF). [f] Reaction with 0.2 mol % of the catalyst.

Ito, Y.; Sawamura, M.; Hayashi, T. *Tetrahedron Lett.*. **1987**, 28, 6215

Gold-Catalyzed Aldol Reactions





(*R,S*)-**4** $R^1 = Me$, $R^2 = H$, $L^1 = PPh_2$, $L^2 = H$
(*S,R*)-**4** $R^1 = H$, $R^2 = Me$, $L^1 = H$, $L^2 = PPh_2$
(*R,R*)-**4** $R^1 = Me$, $R^2 = H$, $L^1 = H$, $L^2 = PPh_2$
(*S,S*)-**4** $R^1 = H$, $R^2 = Me$, $L^1 = PPh_2$, $L^2 = H$

center plane

Entry	Ligand	% **2** [% ee]	% **3** [% ee]
1	(R)-(S)-**4**	89.6 [91 (4S,5R)]	10.4 [7 (4S,5S)]
2	(S)-(S)-**4**	83.5 [41 (4R,5S)]	16.5 [20 (4S,5S)]
3	(S)-(R)-**4**	89.6 [90 (4R,5S)]	10.4 [12 (4R,5R)]

Pastor, S.D.; Togni, A. *J. Am Chem. Soc.* **1989**, *111*, 2333

Gold-Catalyzed Aldol Reactions

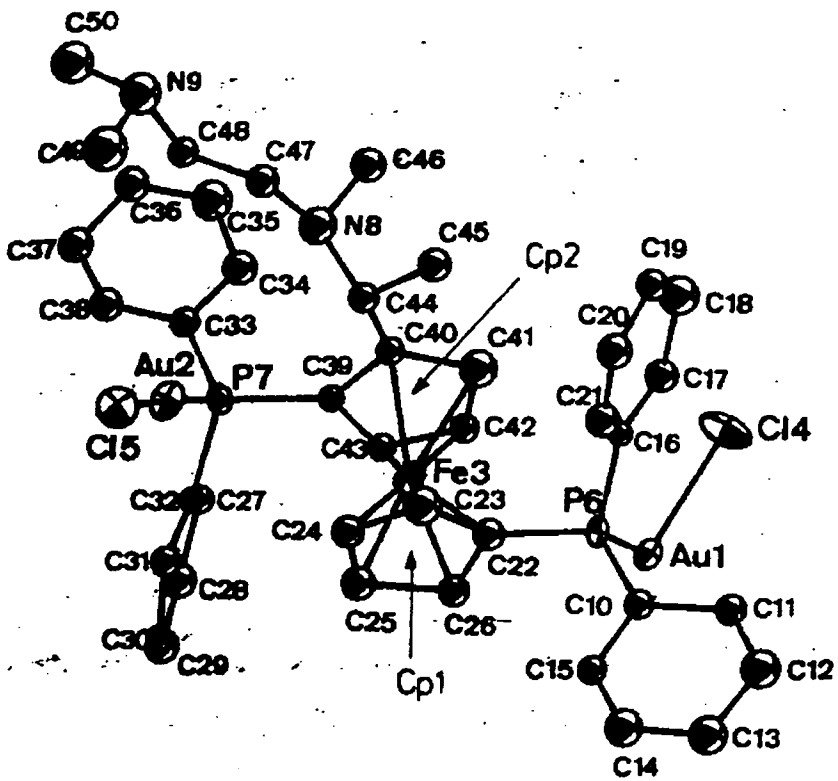


Fig. 1. ORTEP-view [8] of complex 7 showing one of the two symmetry related units and the numbering scheme; thermal ellipsoids are at the 20% probability level. Relevant bonding paran Au(1)–Cl(4) 2.52(3), Au(1)–P(6) 2.31(2), Au(2)–Cl(5) 2.28(2) and Au(2)–P(7) 2.20(2) Å; P(6)–Au(1)- 34(2), P(6)–Au(1)–Cl(4) 113(2) and P(7)–Au(2)–Cl(5) 177(2).

Pastor, S.D.; Togni, A. *J. Orgmet. Chem.* **1990**, *381*, C21

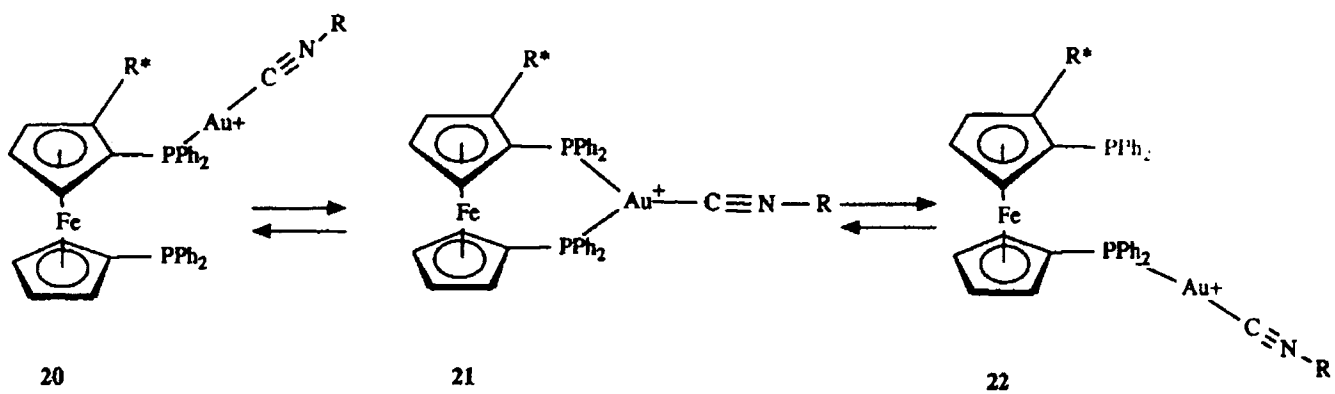
Gold-Catalyzed Aldol Reactions

Variable temperature P31 NMR

- Uncomplexed ligand shows two singlet resonances (δ -23.5 , -17.0)
- Ligand coplexed to Au(I) shows an AB quartet (δ33.0, J = 90.3Hz)
- Addition of excess α-isocyanoacetate ester broadens peak to a singlet
- Addition of excess benzaldehyde gives no change to the AB quartet

Hammet study

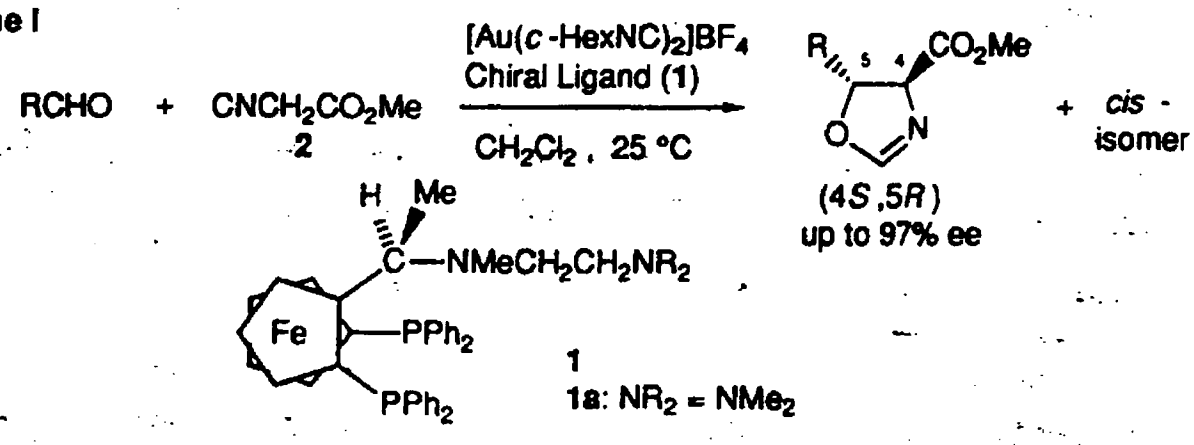
- LFER of ρ=1.4 with para-substituted benzaldehydes

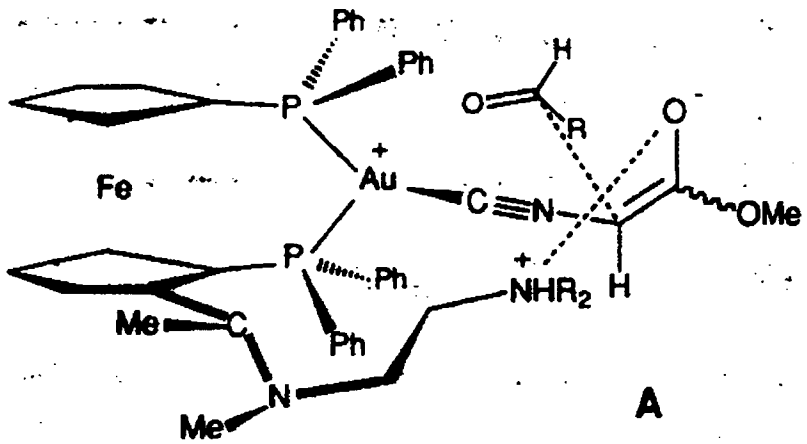


Pastor, S.D.; Togni, A. *J. Org. Chem.* **1990**, *55*, 1649

Gold-Catalyzed Aldol Reactions

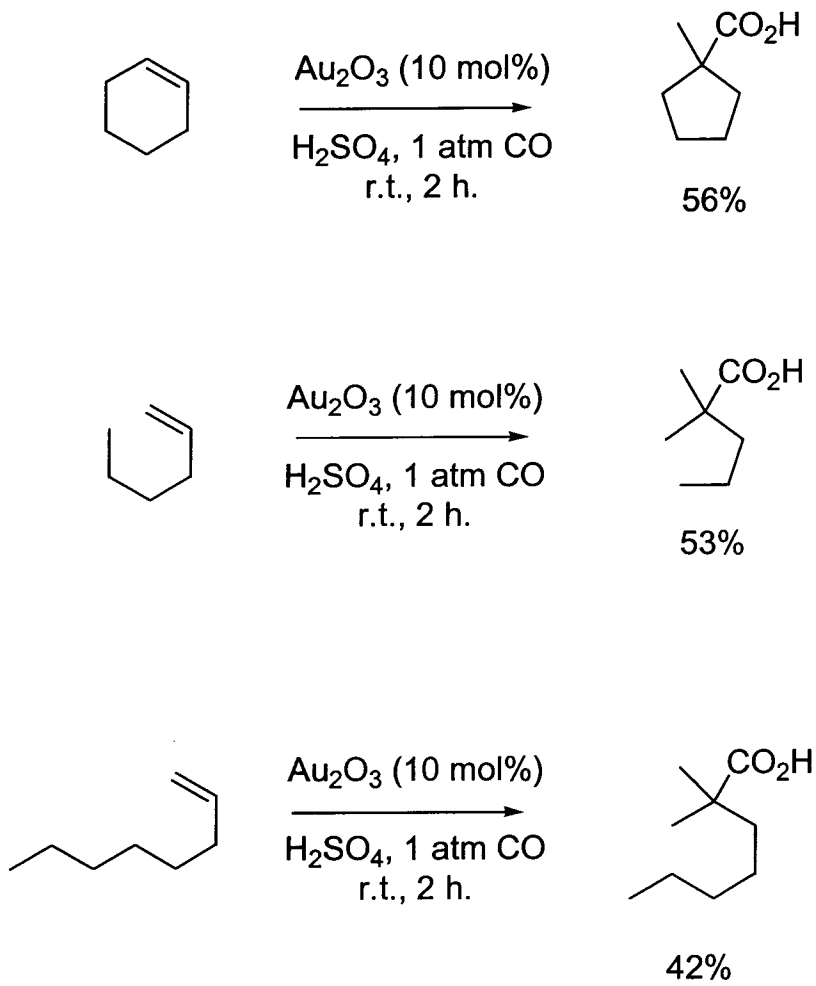
Scheme I

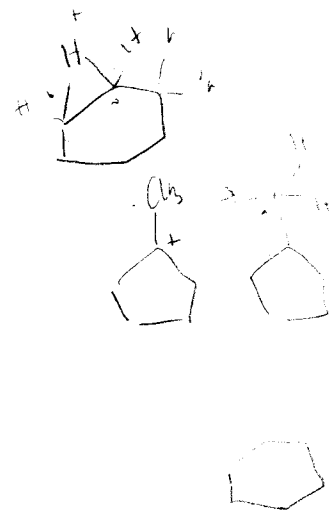




Pastor, S.D.; Togni, A. *J. Org. Chem.* **1990**, *55*, 1649

Gold-Catalyzed Carbonylations of Olefins

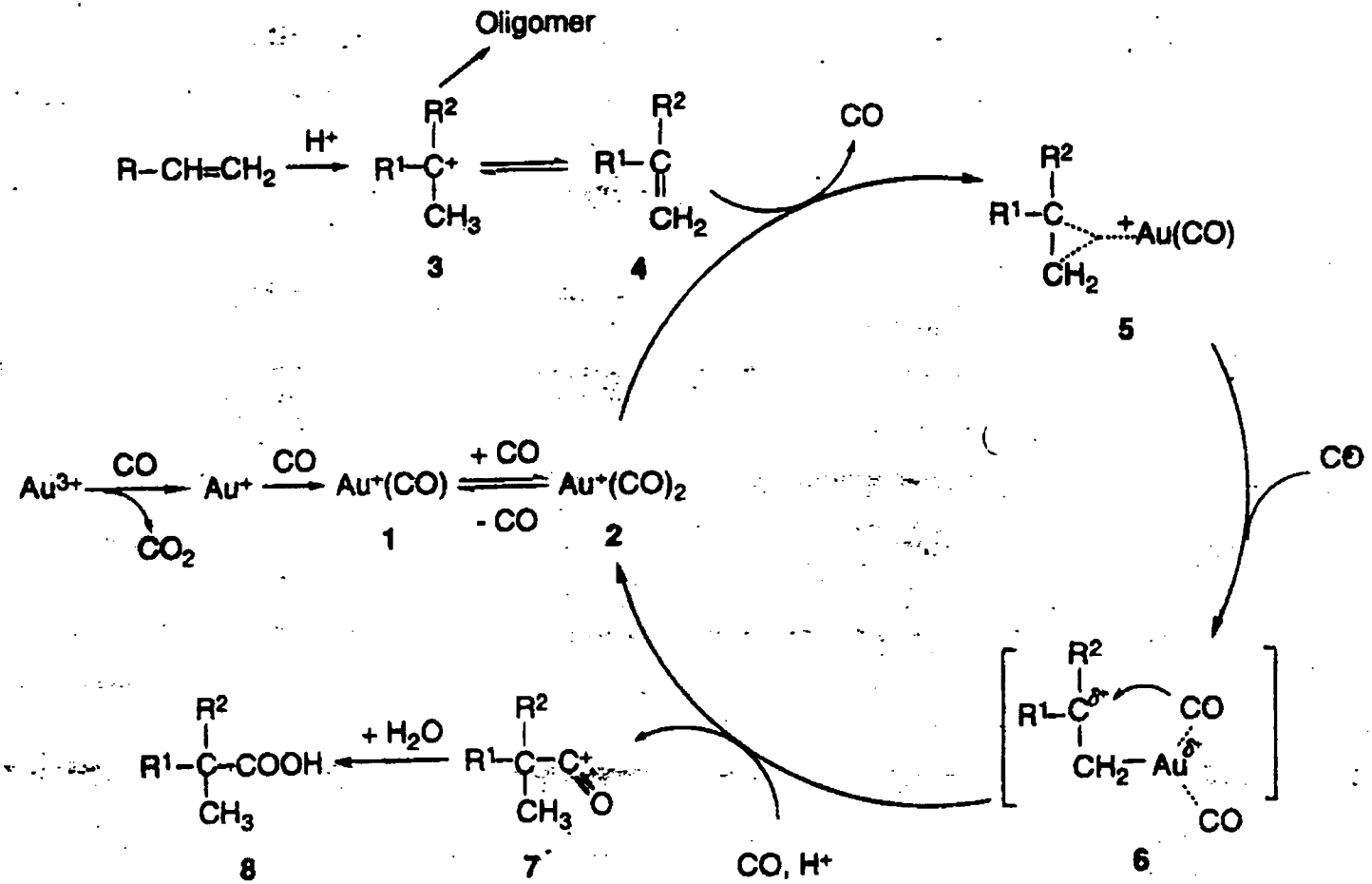




Xu, Q.; Imamura, Y.; Fujiwara, M.; Souma, Y. . *J. Org. Chem.*. **1997**, *62*, 1594

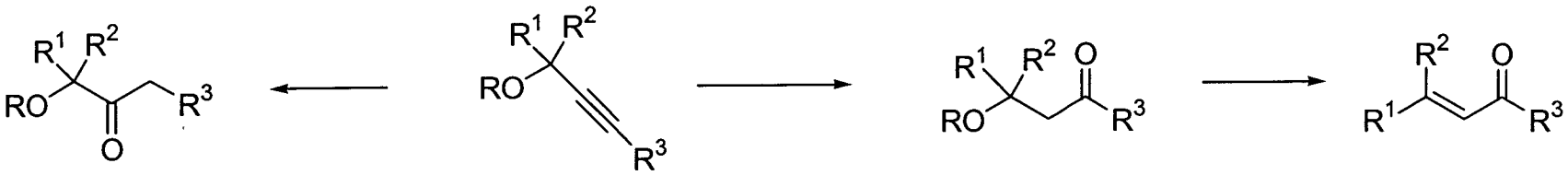
Gold-Catalyzed Carbonylations of Olefins

Scheme 1



Xu, Q.; Imamura, Y.; Fujiwara, M.; Souma, Y. . *J. Org. Chem.*. **1997**, *62*, 1594

Gold-Catalyzed Transformations



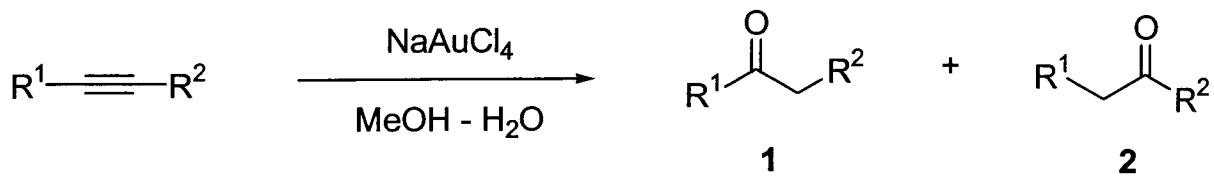
2 **1** **3** **4**

Entry	R^1	R^2	R^3	Reaction time (h)	Product[a]	Yield
1	n-C_5H_{11}	H	n-C_5H_{11}	2	4	79%
2	n-C_5H_{11}	H	CH_3	2	4	75%
3	C_2H_5	H	Ph	10	4	21%
4	CH_3	CH_3	n-C_6H_{13}	10	4	70%
5			CH_3	10	4	30%
6	H	H	n-C_5H_{11}	5	3	91%
7	n-C_5H_{11}	H	H	1	2	91%

a) MeOH contained 10% H_2O

Utimoto, K.; Fukuda, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013

Gold-Catalyzed Transformations

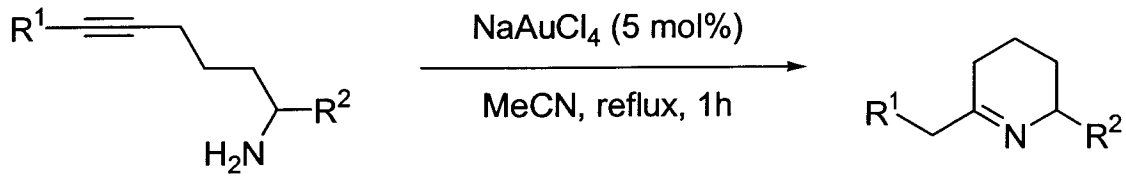


Entry	R^1	R^2	Time (h)	Yield (Ratio **1/2**)
1	*n*-C_6H_{13}	H	1	91%
2	Ph	H	1	91%
3	$HO(CH_2)_9$	H	1	91%
4	$C_5H_{11}CH(OAc)$	H	1	96%
5	*n*-C_6H_{13}	CH_3	5	94% (40/60)

Entry	R^1	R^2	Time (h)	Yield (Ratio **3/4**)
1	*n*-C_6H_{13}	H	1	85%
2	Ph	H	1	96%
3	*n*-C_6H_{13}	*n*-C_6H_{13}	10	93%

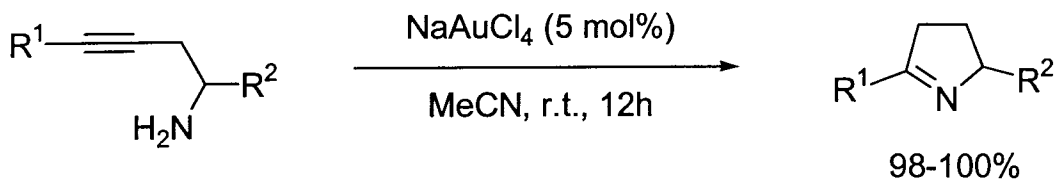
Utimoto, K.; Fukuda, Y. *J. Org. Chem.*. **1991**, 56, 3729

Gold-Catalyzed Amination Alkynes



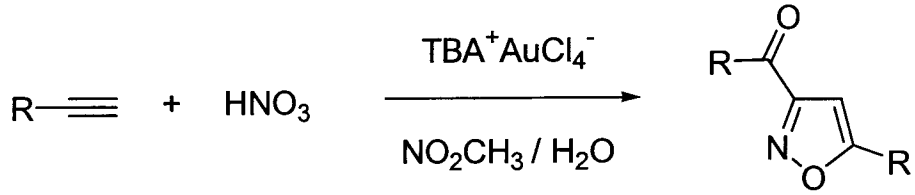
Entry	R^1	R^2	Yield
1	*n*-C_6H_{13}	H	80
2	Et	H	64
3	*n*-C_5H_{11}	Me	71
4	H	*n*-C_6H_{13}	72
5	Ph	H	0[a]

a) Starting material was consumed but no cyclized product was isolated

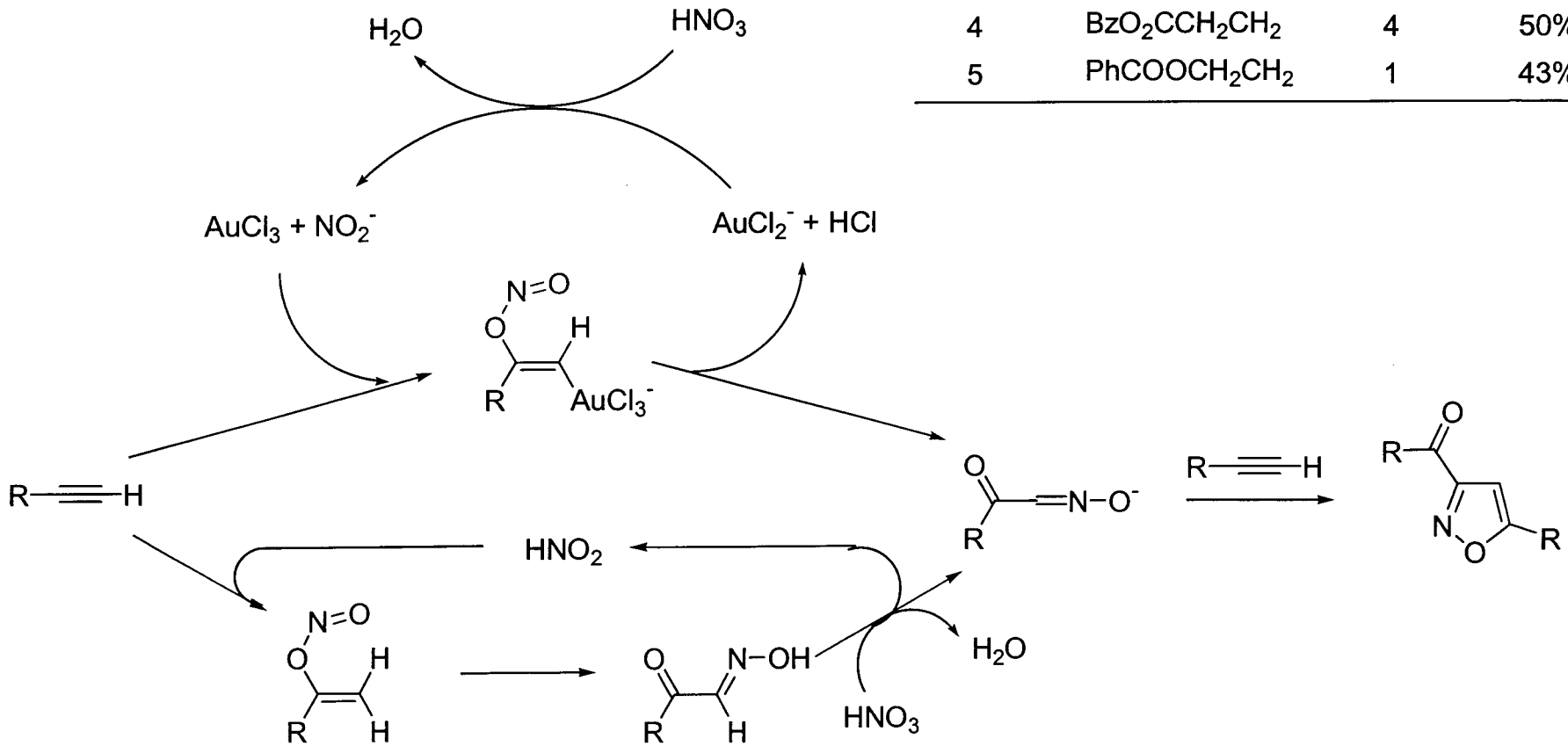


Utimoto, K.; Fukuda, Y. *Synthesis* **1991**, 975

Gold-Catalyzed [2+2+1]

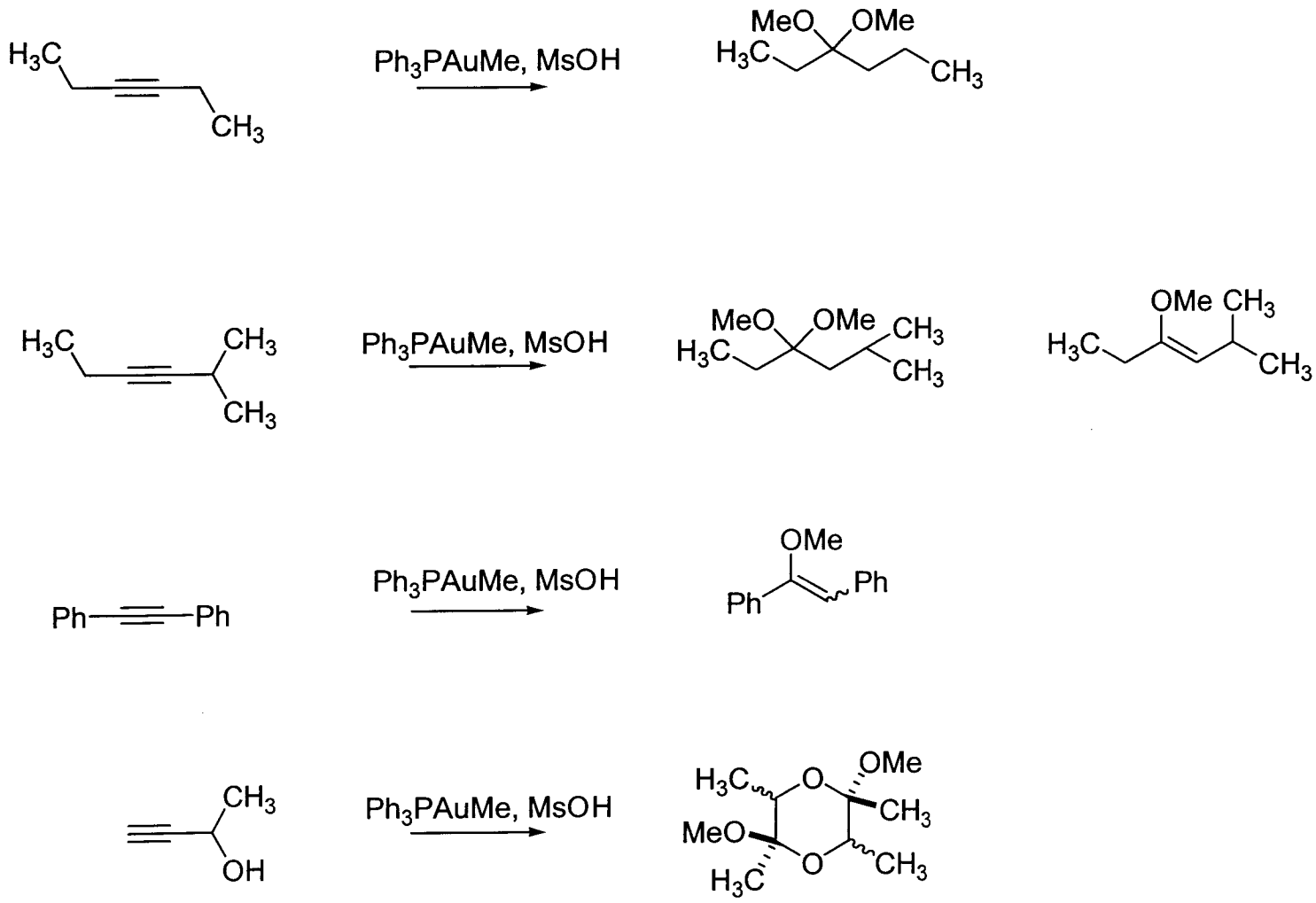


Entry	R	Time	Yield
1	Ph	5	40%
2	n-C_4H_9	1	38%
3	$BzOCH_2CH_2$	5	37%
4	$BzO_2CCH_2CH_2$	4	50%
5	$PhCOOCH_2CH_2$	1	43%



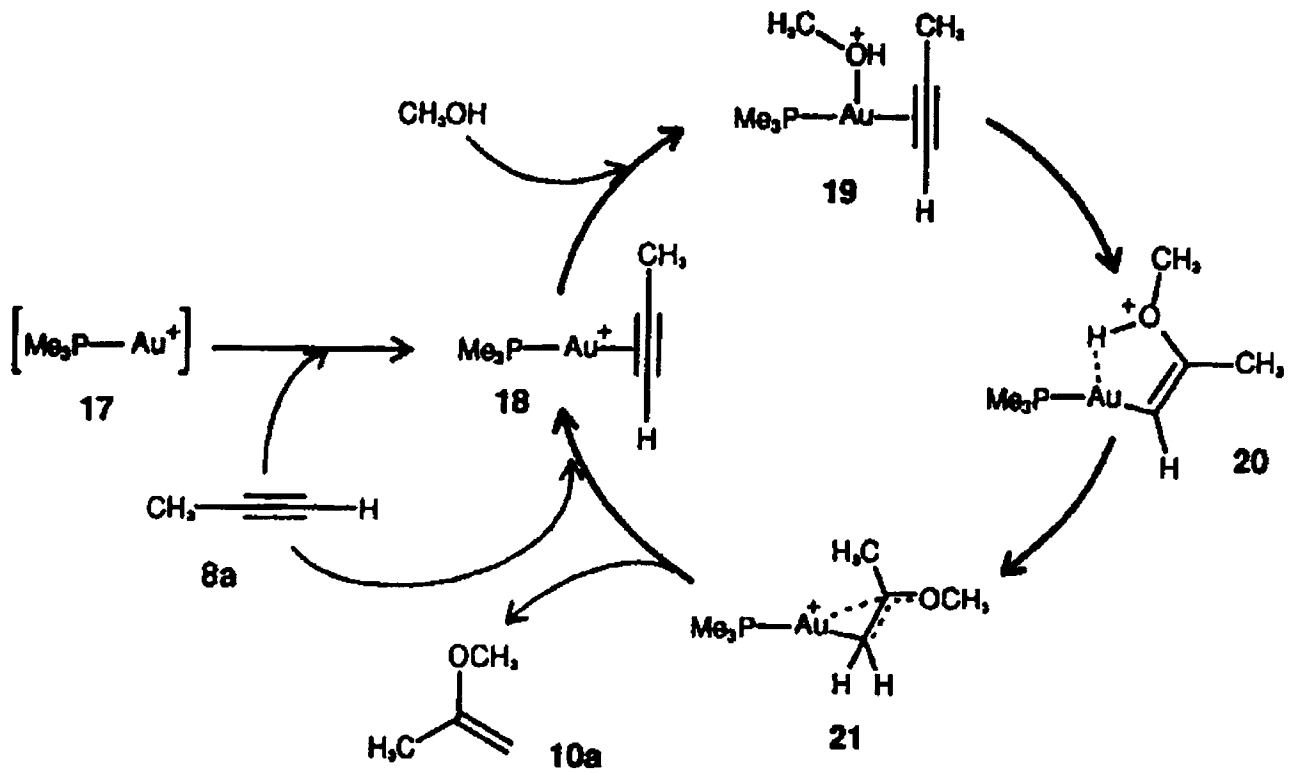
Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; <aresca, L. *J. Am. Chem. Soc.* **1993**, *115*, 4401

Gold-Catalyzed Addition to Alkynes



Teles, J.H.; Brode, S.; Chabanas, M. *Angew. Chem. Int. Ed.* **1998**, 37, 1415

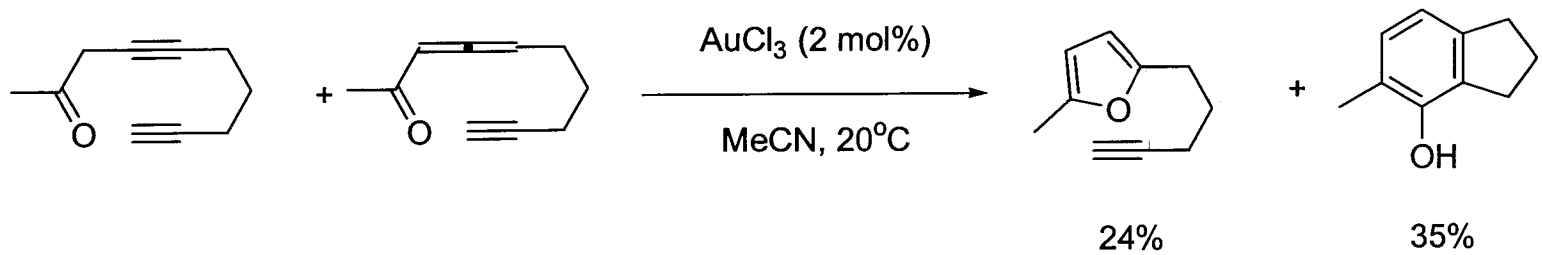
Gold-Catalyzed Addition to Alkynes

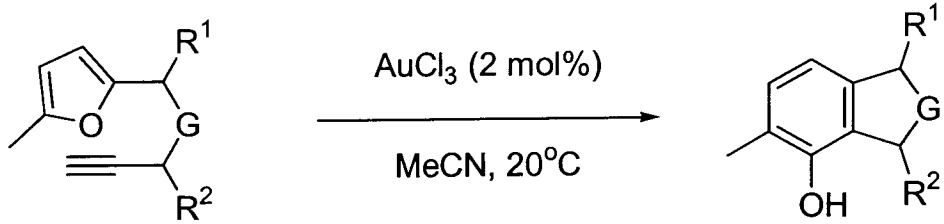


Scheme 3. Proposed mechanism for the addition of methanol to propyne catalyzed by the trimethylphosphanegold(I) cation.

Teles, J.H.; Brode, S.; Chabanas, M. *Angew. Chem. Int. Ed.* **1998**, 37, 1415

Gold-Catalyzed Arene Synthesis



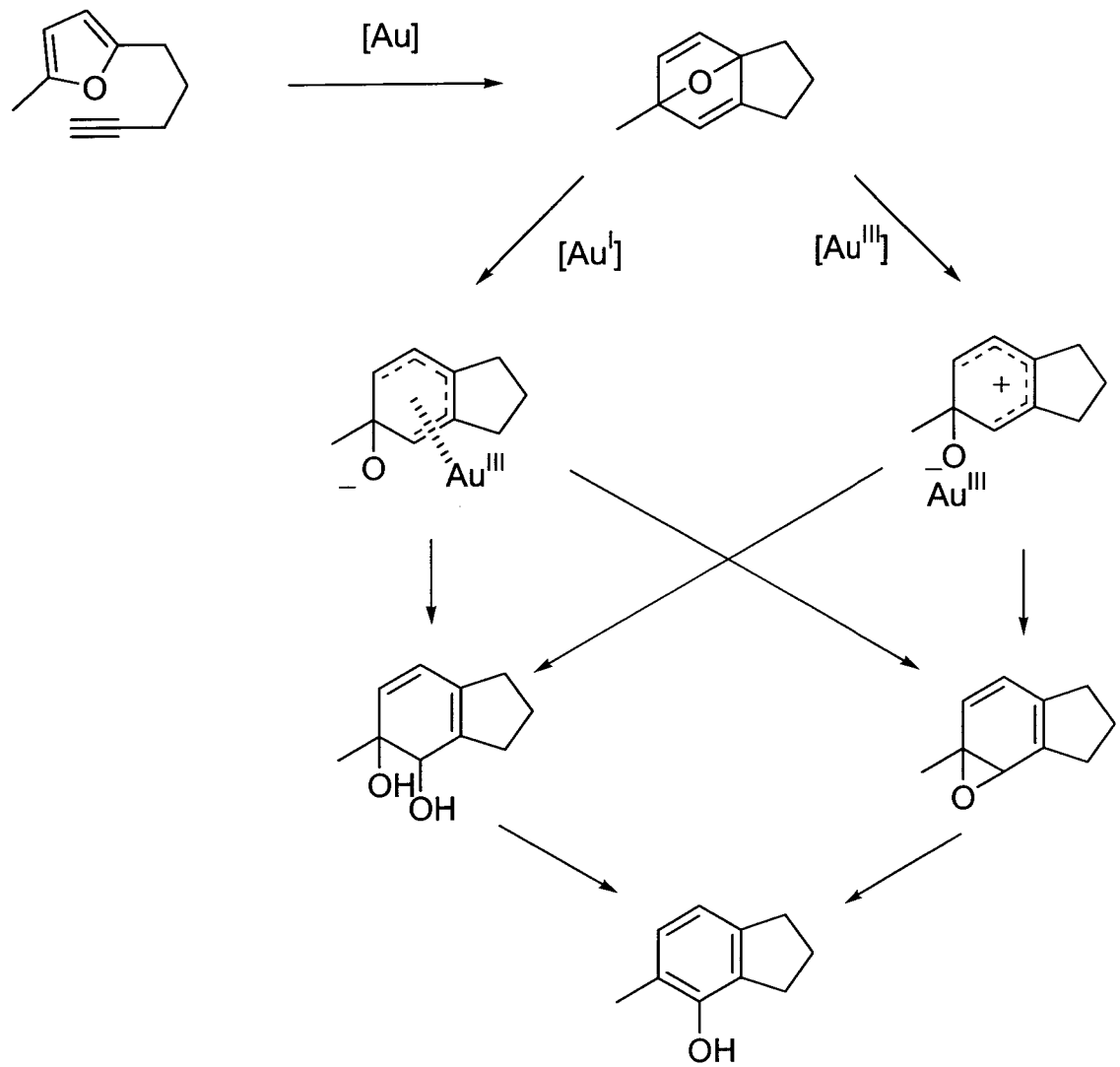


Entry	G	R^1	R^2	Yield
a	CH_2	H	H	65%
b	O	H	H	69%
c	NTs	H	H	97%
d	NTs	Me	H	94%
e	Nts	H	Me	93%
f	NNs	H	H	96%
g	$C(CO_2Me_2)_2$	H	H	88%
h	$N(Ts)CH_2$	H	H	81%[i]

i) 6 mol% $AuCl_3$

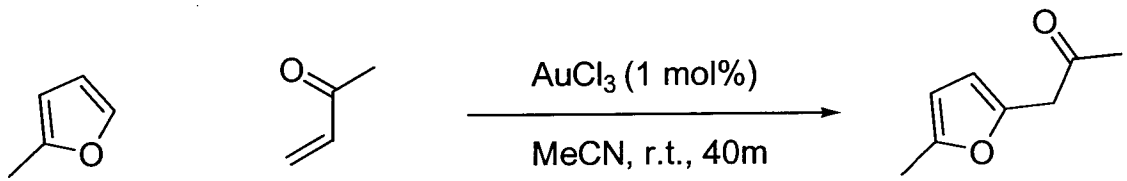
Hashmi, A.S.K.; Frost, T.M.; Bats, J.W. *J. Am. Chem. Soc.* **2000**, *122*, 11553

Proposed Mechanism of Arene Synthesis



Hashmi, A.S.K.; Frost, T.M.; Bats, J.W. *J. Am. Chem. Soc.* **2000**, *122*, 11553

Gold-Catalyzed Michael Additions



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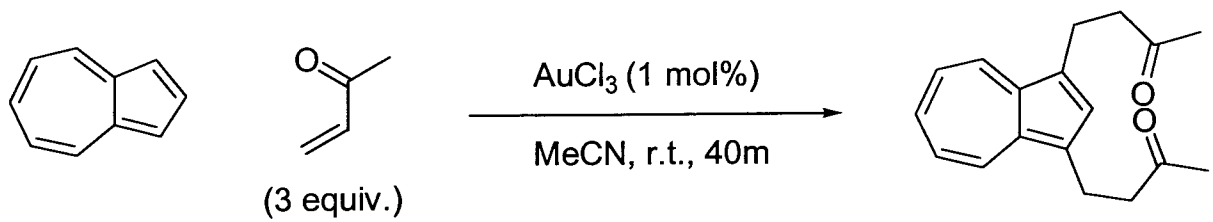

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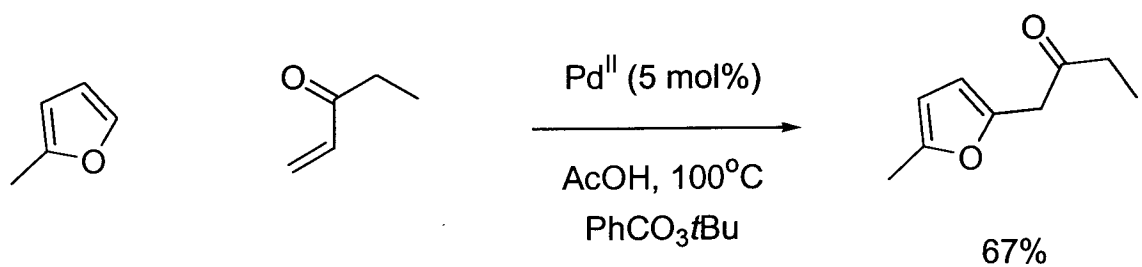

67%

Dyker, G.. *Angew. Chem. Int. Ed.* **2000**, *39*, 4237

Conclusions

- Electronic nature of Au(I) or Au(III) allow for a mesh of metallic qualities from Cu, Ag, and Pd
- The ability of Au to coordinate strongly to alkynes allows for advances in areas relating to their catalytic transformations
- Although the cost of Au is thought to be high, reactions catalyzed by Au are usually found to require small catalytic amounts