The Formation and Reactivity of Gold Carbene Complexes in the Gas Phase.

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Supporting Information

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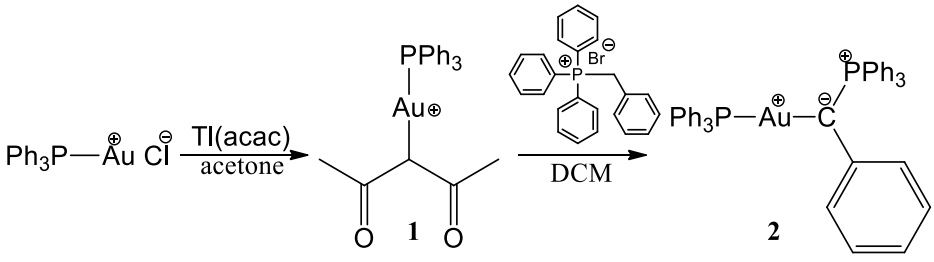
Synthesis of 1,3-diisopropylimidazolium hydrogen carbonate

Using an established method[1], a mixture of 1,3-diisopropylimidazolium chloride (253.91 mg, 1.35 mmol) and $KHCO_3$ (140.60 mg, 1.41 mmol) was dried under a vacuum. Dry methanol (1.25 mL) was then added and mixture stirred for two days at rt. The suspension was then filtered over Celite. The methanol was evaporated under a vacuum to reveal 267.1 mg of a sticky solid (yield varying up to 92%). The sticky solid was triturated with acetone and filtered. The acetone was evaporated under a vacuum leaving a white powder.

Synthesis of 1,3-diisopropylimidazolium gold (I) chloride

Using an established method[1], a mixture of chloro(dimethylsulfide)gold(I) (11.4 mg, 39.0 μmol) and 1,3-diisopropylimidazolium hydrogen carbonate (9.8 mg, 47.0 μmol) was stirred in THF (0.7 mL) for 1 h at 50 °C. The THF was removed under vacuum.

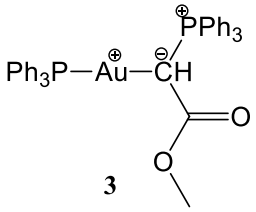
Synthesis of compound 2



Using an established method[2], a mixture of chloro(triphenylphosphine)gold (I) (187.1 mg, 0.4 mmol) and thallium(I) acetylacetonate (128.0 mg, 0.4 mmol) was stirred in 5 mL of acetone

under N_2 for 5 h. The suspension was dried under a vacuum and extracted 4 times (8 mL) with an acetone and diethyl ether mixture (1:15). The extracts were combined, filtered through Celite and dried under a vacuum revealing a white solid **1**. A mixture of compound **1** (6.0 mg, 10.75 μmol) and benzyltriphenylphosphonium bromide (4.4 mg, 10.15 μmol) was stirred in DCM (0.5 mL) at rt for 6 h.

Synthesis of compound 3



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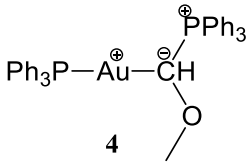
Following the same method used for compound **2**, a mixture of compound **1** (6.68 mg, 11.97 μmol) and (methoxycarbonylmethyl)triphenylphosphonium bromide (5.25 mg, 12.64 μmol) was stirred in DCM (0.5 mL) at rt for 6 h. For mass spec analysis this solution was diluted to 10^{-5} mol/L.

Synthesis of compound 4



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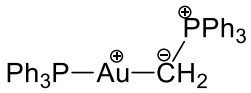
Following the same method used for compound **2**, a mixture of compound **1** (8.25 mg, 14.78 μmol) and (methoxymethyl)triphenylphosphonium bromide (8.05 mg, 20.79 μmol) was stirred in DCM (0.5 mL) at rt for 6 h. For mass spec analysis this solution was diluted to 10^{-5} mol/L.

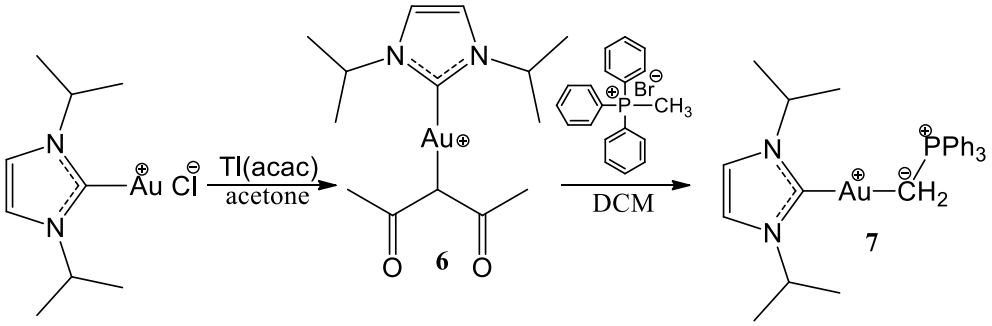
Synthesis of compound 5



5

Following the same method used for compound **2**, a mixture of compound **1** (5.66 mg, 10.14 μmol) and methyltriphenylphosphonium bromide (4.35 mg, 12.18 μmol) was stirred in DCM (0.5 mL) at rt for 6 h. For mass spec analysis this solution was diluted to 10^{-5} mol/L.

Synthesis of compound 7



Following the same method used for compound **2**, a mixture of 1,3-diisopropylimidazolium gold (I) chloride (163.8 mg, 0.4 mmol) and thallium(I) acetylacetonate (126.5 mg, 0.4 mmol) was stirred in 5 mL of acetone under N_2 for 5 h. The suspension was dried under a vacuum and extracted 4 times (8 mL) with an acetone and diethyl ether mixture (1:15). The extracts were combined, filtered through Celite and dried under a vacuum revealing a white solid **1**. A mixture of compound **6** (8.17 mg, 18.22 μmol) and methyltriphenylphosphonium bromide (6.49 mg, 18.17 μmol) was stirred in DCM (0.5 mL) at rt for 6 h. For mass spec analysis this solution was diluted to 10^{-5} mol/L.

Reference 36

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, T.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austrin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian09, Revision C.01* Gaussian Inc., Wallingford CT, 2009.

Computational Data

Me_3PAu^+
Enthalpy M06/QZVP = -596.506413
Electronic Energy M06/QZVP = -596.629806101
Enthalpy Correction LANL2DZ = 0.125603

Au 0. 0. 2.7607857968
P 0. 0. 0.486317418
C -0.8372618283 -1.4501800047 -0.166542507
H -0.3360082856 -2.3549781911 0.1702978748
H -0.8119511517 -1.4063406274 -1.2564209725
H -1.8714668147 -1.4684807831 0.1702978748
C 1.6745236382 -0.0000000106 -0.166542507
H 2.2074750816 0.8864973844 0.1702978748
H 1.6239022854 -0.0000000102 -1.2564209725
H 2.2074750704 -0.8864974123 0.1702978748
C -0.83726181 1.4501800153 -0.166542507
H -0.3360082559 2.3549781954 0.1702978748
H -1.8714667962 1.4684808067 0.1702978748
H -0.8119511339 1.4063406376 -1.2564209725

$Me_3PAuCHOMe^+$
Enthalpy M06/QZVP = -750.253185
(rocking motion in PMe_3 unit led to small, residual imaginary frequency despite doing optimizations analytical frequencies)

P 2.0660331363 1.273402814 -1.1002016418
C 3.0539047484 0.5631720531 -2.4374905538
H 3.7392699835 1.3158593456 -2.8272784335
H 2.4020232514 0.2222046527 -3.2389506181
H 3.6255383542 -0.2855203326 -2.0680922885
C 3.2736692397 1.9166468118 0.0816212803
H 3.9498306418 2.6072571605 -0.4225518348
H 3.8496958999 1.0979962506 0.5076444893
H 2.7624817393 2.4397368274 0.8869767216
C 1.2956068861 2.7405485672 -1.822696799
H 0.6084235673 2.4475820518 -2.6135265475
H 2.0659166239 3.3903480948 -2.2380343402
H 0.7404918516 3.2833883236 -1.060827123
Au 0.5235917118 -0.2357052666 -0.1605294184
C -0.8180027882 -1.5512547162 0.6895043793
H -0.9739399561 -1.6486871789 1.7772540893
O -1.5416602388 -2.3273929568 0.0131830489
C -2.4779631594 -3.2478311657 0.6329001733
H -2.1901613401 -4.2454998472 0.3192734443
H -3.4611979794 -3.0013594067 0.2468836004
H -2.4345000422 -3.1405478054 1.7146835221

$Me_3PAuCHMe^+$
Enthalpy M06/QZVP = -675.009613
(rocking motion in PMe_3 unit led to small, residual imaginary frequency despite doing optimizations analytical frequencies)

P 1.1096690648 1.1133733681 -0.4527891059
C 1.9812812821 0.3237855903 -1.8255269674
H 2.7168791531 1.0145513891 -2.2376838641
H 1.2737702642 0.0471689486 -2.6042911042
H 2.488313931 -0.5741977927 -1.479166673
C 2.4086999727 1.6511939075 0.6833854439
H 3.1210966007 2.2837425505 0.1536896248
H 2.9302625209 0.7870687432 1.0893202022
H 1.9724158428 2.2137937082 1.5060022688
C 0.4329217737 2.6402141869 -1.1458722803

H -0.3072628555 2.4071831264 -1.9082540587
H 1.2372195701 3.2246509266 -1.5927604936
H -0.0435877629 3.2260871982 -0.3628978844
Au -0.5316492051 -0.2614613107 0.5627601772
C -1.9145191378 -1.4469777001 1.4605679955
H -2.0194571864 -1.4138148737 2.5485712647
C -2.8790108513 -2.3117936896 0.8488341712
H -3.7424246496 -1.6040373999 0.8786655792
H -2.7151793913 -2.5610943751 -0.1944804414
H -3.2130922861 -3.1551945698 1.4543860295

$Me_3PAuCHOMe^+$ TS to acetaldehyde complex
Enthalpy M06/QZVP = -750.161665
Imaginary frequency = -729.0327 cm^{-1}

Au -0.8578963371 0.4382506852 0.4225052379
P 1.2609465062 -0.1123109167 -0.4089299403
C 2.3056395087 -0.9542786135 0.7994704192
H 2.436483078 -0.3253997927 1.6774976479
H 3.280207913 -1.161909995 0.3572367936
H 1.8431236676 -1.8902235656 1.1050790537
C 2.2011630384 1.3404920227 -0.9246196221
H 2.3361118794 2.0140061412 -0.0810066017
H 1.6683220946 1.8683951808 -1.7125842002
H 3.1777863937 1.0300716376 -1.2964072272
C 1.2261065902 -1.1963628089 -1.8541194476
H 0.7438212542 -2.1382981807 -1.6020984285
H 2.2457334114 -1.3930314681 -2.186489562
H 0.6716973963 -0.7221607572 -2.6610156632
C -2.6517413197 1.2094325784 1.3026559687
H -3.0284644861 2.1777453735 0.9157981059
O -3.0428038278 0.8873973496 2.4449074224
C -3.8212533921 -0.1561312159 1.0034969618
H -4.0640916538 0.2940057636 0.0400278728
H -4.6745239904 -0.1363150682 1.6694503552
H -3.2563677249 -1.0733746162 0.9891448016

Me_3PAu^+ acetaldehyde complex
Enthalpy M06/QZVP = -750.308582

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C 0.1019093139 0.3457840711 -0.9816347645
H 0.7955071398 -0.3567779524 -1.4383742617
H 0.3971249829 1.3632748156 -1.2392051623
H -0.8973198389 0.1525659742 -1.3656228612

C -0.961070051 1.446910645 1.4508861089
H -0.6203747852 2.4167389963 1.0874777673
H -0.9426519997 1.4441273851 2.5385210102
H -1.9817473838 1.2758250742 1.1158858774
C 1.7872749103 0.6135426568 1.3307300261
H 2.5113684486 -0.0831169155 0.9139626236
H 1.8599714533 0.5888441198 2.415718455
H 2.0101346008 1.6203478783 0.9768286822
Au -0.4764396846 -1.9235590847 1.4844643435
C -1.6308415403 -4.2962966438 3.0585114651
H -1.9801741743 -3.5618687961 3.8006153435
O -1.0217549835 -3.9214898176 2.0706538416
C -1.9301910831 -5.7092852092 3.3163813657
H -1.5462329651 -6.3520617124 2.5309372331
H -3.0109751134 -5.8295074832 3.4191547257
H -1.5094395437 -5.9898919409 4.2845370416

CHOMe
Enthalpy M06/QZVP = -153.641017

C 0.4524153189 -0.4677832952 -0.4158262135
H 1.3120975207 -0.3919127147 0.2462615408
H 0.76095359 -0.6402232366 -1.4434543641
H -0.2201149883 -1.2602545289 -0.0984508224
O -0.2739018393 0.7667094452 -0.3772233668
C 0.194367384 1.691443603 0.3881216029
H -0.5339017389 2.5233541953 0.2391012332

MeOMe
Enthalpy M06/QZVP = -154.915497

C 0.0142846096 -0.0082472122 -0.7991450265
H -0.8462878204 -0.5363671304 -1.2283977171
H 0.9240907886 -0.5335241132 -1.0796780795
H 0.0413638056 1.0010903667 -1.228397629
O -0.0524744306 0.0302960634 0.5933694991
C -1.197068068 0.6911275764 1.0408493759
H -1.2219075701 1.7306196841 0.6914667903
H -1.1870614128 0.6853501683 2.1280078148
H -2.1097144353 0.1928933049 0.6914667022

Ethane
Enthalpy M06/QZVP = -79.717079

C 2.1477992296 -0.8075603468 0.5718447658
H 3.0939795042 -0.6458791938 0.0575747141

H 2.101536028 -1.8597000898 0.8489574784
H 2.1727267891 -0.2272918359 1.4929802699
C 0.9708948078 -0.4127509202 -0.298269855
H 1.0170361793 0.6394401101 -0.5748882505
H 0.0248866457 -0.574854144 0.2160140377
H 0.9461763383 -0.9926413106 -1.2195310824

MeCH
Enthalpy M06/QZVP = -78.391289

H 0.0417270398 0.0178792252 -0.0325581819
C -0.1137734523 -0.0158696394 1.0498281071
H 0.9011047998 -0.1496454472 1.505905259
H -0.4905653422 0.9256462276 1.4462204785
C -0.5714600186 -1.2156242741 1.7052006069
H -0.2817923895 -2.0600531451 1.0514167813

Me_3PAu^+ complex with trans-1,2-diphenylcyclopropane
Electronic Energy M06/QZVP = -1176.48233568
Enthalpy Correction LANL2DZ = 0.386764

C -0.5711600977 -2.0207251074 -0.5988502004
H -0.234196962 -1.7436434055 -1.592909386
C -1.9791419361 -1.6520462394 -0.289317787
C -4.6260975113 -0.9357497749 0.2097777668
C -2.7307493521 -0.9931395519 -1.2586881567
C -2.5738884827 -1.9519260919 0.9312375562
C -3.8867513759 -1.593549275 1.178329435
C -4.0450479283 -0.639973948 -1.0112405441
H -2.2818849194 -0.7683241552 -2.2192025639
H -2.0175330267 -2.4737116593 1.7003565855
H -4.3367720768 -1.8365704571 2.1304510893
H -4.6198074573 -0.1409523996 -1.7788817599
H -5.6539251508 -0.6641194571 0.4028108382
Au 0.0779007461 0.3650667111 0.0366285916
P -0.0881363545 2.6291992214 0.0148409808
C -1.6283198525 3.1903246525 -0.7399182671
H -1.6692363421 4.2798153607 -0.733983018
H -2.4742360348 2.7900082011 -0.1842955069
H -1.6865247634 2.8310688371 -1.7655041058
C -0.0534370921 3.3725527821 1.6584673047
H -0.8744295161 2.986319957 2.2583008067
H -0.1493080926 4.4549147602 1.5687293364
H 0.8859556787 3.1338828334 2.1521758216
C 1.2348494142 3.4391948066 -0.9061970956
H 1.0898741304 4.5195107912 -0.8783445711

H 1.2288460618 3.1009339006 -1.9399528292
H 2.1969583964 3.1909210264 -0.4628421704
C 0.0173454635 -3.2829610172 -0.0905959061
H 0.679591446 -3.825571203 -0.750178735
H -0.6224118203 -3.8960254079 0.5279290131
C 0.5766135086 -2.0465110474 0.5224037555
H 0.2292485394 -1.8625836851 1.534632341
C 1.985105271 -1.639733982 0.2559011047
C 4.6271556596 -0.8567476888 -0.1589921391
C 2.577319333 -1.785940053 -0.9955668706
C 2.7385716592 -1.1031988738 1.2978315271
C 4.0502121517 -0.7162107461 1.0909932952
C 3.887415724 -1.3944691337 -1.1992439984
H 2.0183766818 -2.209375761 -1.821118945
H 2.2910430209 -0.9982718064 2.278790677
H 4.6251142481 -0.311338706 1.9118408225
H 4.3357772533 -1.5164758233 -2.1750787553
H 5.6528637579 -0.5581253846 -0.3208653375

Me_3PAu^+ complex with styrene (C-P-Au-C dihedral locked)
Enthalpy M06/QZVP = -905.966528
Electronic Energy M06/QZVP = -906.232077102
Enthalpy Correction LANL2DZ = 0.269095

P -2.4217184088 -0.8804745126 0.0076579216
C -3.6201869855 -0.5477599027 -1.3015413497
H -3.9958243402 0.4692786448 -1.2117351447
H -4.4521196812 -1.2475388954 -1.2194958869
H -3.1491668023 -0.6619523327 -2.2753818323
C -3.3602152064 -0.7769854727 1.5475168823
H -3.7281364321 0.2365071171 1.691829364
H -2.7245093332 -1.0420951166 2.3895069754
H -4.205444013 -1.4641470439 1.5042531324
C -1.9961982476 -2.6270270825 -0.1710731061
H -1.4997592341 -2.7925548376 -1.124746473
H -2.9042240769 -3.229044779 -0.1287871595
H -1.3253937462 -2.9295360499 0.6299677399
Au -0.5850044798 0.5397105536 -0.0373836953
C 1.6234562504 1.3771653719 -0.6036004262
H 1.5102237349 1.5419886135 -1.6716452088
C 0.9312357954 2.2099532469 0.2324812947
H 0.4022814531 3.0603500282 -0.1759603513
H 1.1165769285 2.2266240571 1.2989097729
C 2.5823813187 0.3452589671 -0.246389143
C 4.4668350056 -1.6144398231 0.3226149927
C 3.2122263872 -0.3538388468 -1.275710417
C 2.9098372812 0.0442486176 1.0782403548

C 3.8440249115 -0.9278832051 1.3572943116
C 4.1510545107 -1.3269941943 -0.9932991041
H 2.9660667611 -0.1196495296 -2.3036532626
H 2.4377071603 0.5771454692 1.8930947709
H 4.0984824291 -1.1522022744 2.3831463826
H 4.6393876318 -1.8569275255 -1.7981229031
H 5.203388428 -2.3726652628 0.5475355678

trans-1,2-diphenylcyclopropane
Enthalpy M06/QZVP = -579.545779
Electronic Energy M06/QZVP = -579.801860786
Enthalpy Correction LANL2DZ = 0.258493

C -0.6715104691 0.0711405976 0.6084081386
H -0.1526107325 -0.1632945426 1.5326158101
C -1.6769690173 -0.9370387979 0.1806764495
C -3.5496151612 -2.8646897806 -0.5690734884
C -3.0051666722 -0.8268017152 0.5725701676
C -1.3026883831 -2.0266369371 -0.5969744833
C -2.2295558941 -2.9840538944 -0.9692699895
C -3.9357145665 -1.7817700838 0.2021094316
H -3.3077791667 0.0217186536 1.1734356746
H -0.271473874 -2.1174091471 -0.9168854442
H -1.9215436398 -3.8244405181 -1.5764450711
H -4.9660829335 -1.6793298668 0.5144766005
H -4.2757772503 -3.6105199149 -0.8615617048
C -0.904333098 1.5289064307 0.3640237471
H -0.5796364576 2.2288057382 1.1212093582
H -1.8077623931 1.8077205874 -0.1600904871
C 0.1555323492 0.800566109 -0.400973313
H -0.0932860509 0.5782621498 -1.4339528431
C 1.5944762186 1.0756736646 -0.1478237677
C 4.3070797341 1.5828801448 0.2636278607
C 2.4782935756 0.03768296 0.1232673723
C 2.0910491793 2.3718217917 -0.2049222251
C 3.4361144372 2.6258019177 -0.0014128363
C 3.8239365845 0.2869138106 0.3268998358
H 2.1002491949 -0.9761336009 0.1802236816
H 1.4093260245 3.1879230472 -0.4094537781
H 3.8054355659 3.6412770633 -0.0476551483
H 4.4973665919 -0.5324318162 0.5389083191
H 5.3579092835 1.7796679795 0.4253533926

styrene
Enthalpy M06/QZVP = -309.395773
Electronic Energy M06/QZVP = -309.5364529
Enthalpy Correction LANL2DZ = 0.141951

C 0.3068169648 -0.0264811011 1.1893607849
H 0.1867221715 0.83733367 1.8359236864
C 0.5461163476 0.1821462536 -0.0986420977
H 0.6776896234 -0.6251978506 -0.8065604459
H 0.6199137879 1.1836601624 -0.4955388443
C 0.1807570789 -1.3154992121 1.867288657
C -0.076083302 -3.7322513907 3.2487433054
C 0.3038959006 -2.5353919662 1.202856486
C -0.073214569 -1.3368112933 3.236273883
C -0.200793864 -2.531259557 3.9223771237
C 0.177030733 -3.7278955474 1.8847860883
H 0.5014648046 -2.5502823961 0.1393195445
H -0.1710790511 -0.3968459676 3.7653187218
H -0.3980130091 -2.5226609741 4.9855540878
H 0.275715484 -4.6636280556 1.3516985874
H -0.1749448992 -4.6683453103 3.7804843919

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