Published in final edited form as:

Organometallics. 2016 September 12; 35(17): 2938–2943. doi:10.1021/acs.organomet.6b00487.

Synthesis and Properties of “Sandwich” Diimine-Coinage Metal Ethylene Complexes

Kristine Klimovica[†], Kristin Kirschbaum[‡], and Olafs Daugulis^{*,†}

[†]Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States

[‡]Department of Chemistry, University of Toledo, Toledo, Ohio 43606, United States

Abstract

Synthesis and full characterization of cationic isostructural “sandwich” diimine-coinage metal ethylene complexes are reported. Ethylene self-exchange kinetics proceeds by an associative exchange mechanism for Cu and Au complexes. The fastest ligand exchange was observed for Ag complex **8a**. The upper limit of $G^\ddagger$, assuming associative ligand exchange, was found to be ca. 5.0 kcal/mol. Ethylene self-exchange in Cu complex **7b** proceeds with $G_{298}^\ddagger = 12.9 \pm 0.1$ kcal/mol, while the exchange is the slowest in Au complex **9**, with $G_{298}^\ddagger = 16.7 \pm 0.1$ kcal/mol. Copper complex **7b** is unusually stable and can survive in air for years.

Graphical abstract

1. INTRODUCTION

Transition-metal-alkene complexes are important intermediates in catalysis. Many processes, such as olefin polymerization, hydrogenation, metathesis, and cyclopropanation, involve the intermediacy of metal-alkene complexes.^{1,2a} The olefin complexes of group 11 metals are less common and become increasingly rare moving from copper to silver to gold despite their importance in cyclopropanation and carbon–hydrogen bond functionalization.² In fact, the first gold-ethylene complex was structurally characterized only recently.³ Furthermore, direct comparison of all three coinage metal-ethylene complexes is difficult, as very few have been synthesized with analogous supporting ligands.⁴ Ligand exchange kinetic data

*Corresponding Author: (O. Daugulis): olafs@uh.edu.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00487. Detailed experimental procedures, kinetic calculations, and characterization data for new compounds (PDF) Crystallographic data (CIF)

Notes

The authors declare no competing financial interest.

have not been obtained for isostructural group 11 metal olefin complexes. Moreover, few monomeric cationic coinage metal-ethylene complexes have been crystallographically characterized.^{4a–e,5}

We have developed a general synthesis of 8-aryl-1-naphthylamines based on C–H bond functionalization.⁶ In collaboration with the Brookhart and Coates groups, palladium and nickel complexes of “sandwich” diimines derived from 8-aryl-1-naphthylamines were used for olefin polymerization (Figure 1).⁷ Interestingly, complex **2a** catalyzes living polymerization of ethylene at room temperature. This was attributed to the increased axial steric bulk provided by the capping arene groups.^{7b} Consistent with living polymerization and increased axial bulk, the rate of associative ethylene exchange in **2b** is exceedingly slow compared to other palladium diimine systems.^{7b}

The axial aryl substituents on the ligand provide steric protection for the coordinated metal center and substantially retard associative ligand exchange. We speculated that coinage metal “sandwich” diimine complexes with ethylene should possess increased stability. We report here the synthesis, characterization, and ethylene exchange kinetics of “sandwich” diimine copper, silver, and gold complexes.

2. SYNTHESIS OF COMPLEXES

2A. Ligand Synthesis

8-(3,5-Dichlorophenyl)naphthalen-1-amine was synthesized by using C–H bond functionalization methodology developed earlier.⁶ The synthetic procedure is summarized in Scheme 1. Picolinic acid 1-naphthylamide was coupled with 3,5-dichloriodobenzene to yield *N*-(8-(3,5-dichlorophenyl)-naphthalen-1-yl)picolinamide (**4**) in 77% yield. The reaction is easily scalable and can be performed on at least an 80 mmol scale. The reaction requires a Pd(OAc)₂ catalyst, AgOAc as a base, and a halide removal agent and proceeds in the absence of solvent. Amide hydrolysis yields 8-(3,5-dichlorophenyl)naphthalen-1-amine (**5**). Synthesis of 2,3-butanedione diimine ligand **6** was accomplished in 86% yield.

2B. Synthesis and Properties of Copper Complexes **7a** and **7b**

Treatment of a dichloromethane solution of ligand **6** with (CuOTf)₂PhH in the presence of ethylene afforded triflate **7a** in 85% yield as a red solid (Scheme 2). The corresponding hexafluoroantimonate salt **7b** was synthesized by the reaction of Cu(C₂H₄)₃SbF₆^{4a} with **6** in ethylene-saturated CH₂Cl₂. Complex **7b** was obtained in 81% yield as an orange solid after crystallization by layering pentane over the solution of **7b** in CH₂Cl₂ at –20 °C. Pure **7a** and **7b** are relatively stable and can be stored outside the glovebox at room temperature under an inert atmosphere for years without any signs of decomposition, as evident by ¹H NMR spectroscopy and single-crystal crystallography. Furthermore, solid **7b** is stable if kept on the bench under air for years, and it does not lose complexed ethylene if kept under vacuum for at least 30 min. The unusual stability of **7a** and **7b** relative to other known Cu-ethylene complexes may be related to steric protection provided by the axially positioned aryl groups on the ligand.

Complexes **7a** and **7b** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of **7a** in CDCl_3 shows a broad resonance centered at 4.01 ppm that is assigned to the signal of the ethylene ligand protons. In contrast, complex **7b** shows two resolved signals for ethylene protons at 4.01–3.93 (m, 2H) and 3.86–3.77 ppm (m, 2H) in CD_2Cl_2 . A carbon-13 signal for complexed C_2H_4 was not observed in the ^{13}C NMR spectra of **7a** from -20 to $+40$ °C. However, the shift for bound C_2H_4 can be located using 2D-HMQC NMR spectra, and it appears at 88.9 ppm. For **7b**, the bound ethylene signal in the ^{13}C spectrum appears at 88.0 ppm. The assignment of the signal was verified by 2D-HMQC NMR spectra. The complexed ethylene signals in the ^1H and ^{13}C spectra are substantially upfield compared with those of other monomeric cationic copper-ethylene complexes and are similar to shifts observed in neutral complexes.^{4a,f,5,8}

Crystals of **7a** suitable for X-ray analysis were grown by layering Et_2O over the solution of the complex in CH_2Cl_2 at -20 °C. The ORTEP diagram of complex **7a** is shown in Figure 2. The solid-state structure of **7a** shows an ethylene ligand coordinated to copper in a typical η^2 fashion. Ethylene is nearly coplanar with the α -diimine ligand and the ligand chelates the copper ion with a bite angle of $81.94(16)^\circ$. The complexed ethylene $\text{C}=\text{C}$ distance is $1.346(8)$ Å, which is slightly lengthened compared to the $\text{C}=\text{C}$ distance of free ethylene (1.337 Å) and is fairly typical for the values observed in other copper(I)-ethylene complexes with bidentate nitrogen-donating ligands.^{4f,5} The $\text{Cu}-\text{C}(\text{ethylene})$ distances for **7a** are $1.972(5)$ and $2.016(5)$ Å. The aryl groups of the ligand are centered over the five-membered chelate ring. Interestingly, the *ortho*-carbons of the dichlorophenyl groups (C22, C38) show a relatively close approach to Cu(1) at 3.17 and 3.14 Å.

2C. Synthesis and Properties of Silver Complexes **8a** and **8b**

Silver-ethylene complexes are substantially rarer than the corresponding copper complexes, presumably due to their instability that is caused by the more oxidizing nature of Ag(I) and weaker binding of olefins to Ag.⁹ Reaction of AgSbF_6 with ligand **6** in the presence of ethylene in CH_2Cl_2 at -75 °C afforded complex **8a** as a dark orange, air-, temperature-, and light-sensitive solid (Scheme 3). It decomposes at room temperature within 1 day as a solid and within a few hours in solution under an inert atmosphere. It can be stored for several months as a solid under an inert atmosphere at -20 °C. The corresponding tetrafluoroborate complex **8b** was obtained similarly in 88% yield as an orange-brown, sensitive solid.

Complexes **8a** and **8b** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The signal of the ethylene ligand protons appears as a singlet at 4.94 ppm in CDCl_3 (**8a**) or CD_2Cl_2 (**8b**) solvents. Carbon-13 signals for complexed C_2H_4 appear at 105.4 (**8a**) and 105.9 (**8b**) ppm. The assignment of complexed ethylene ^{13}C signals was verified by DEPT-135 or 2D-HMQC experiments. The complexed ethylene signals in ^1H and ^{13}C spectra are shifted somewhat upfield compared with those observed for other monomeric cationic silver-ethylene adducts.^{4a-c,f} However, the dearth of well-characterized cationic Ag complexes and their structural differences with **8** do not allow for meaningful comparisons.

Crystals of **8b** suitable for X-ray analysis were grown by layering methylcyclohexane over the solution of **8b** in CH_2Cl_2 at -20 °C. The ORTEP diagram of **8b** is shown in Figure 3.

The bound ethylene C=C bond length is 1.348(10) Å, which is slightly lengthened compared to the C=C distance of free ethylene (1.337 Å), and falls within the values expected for silver-ethylene complexes. Less than 20 silver-ethylene complexes have been structurally characterized.^{4a-c,10,11} Among them, the only examples of cationic complexes are tris(ethylene)Ag cations reported by Dias and Krossing.^{4a-c}

2D. Synthesis and Properties of Gold Complex 9

Well-characterized gold-ethylene adducts are particularly rare. Only six complexes appear to be characterized by X-ray crystallography.^{3,4d-f,12} Specifically, three fluorinated Tp-Au(ethylene) complexes and one complex supported by a fluorinated triazapentadiene have been reported by Dias.^{3,4f,12} Two Au(C₂H₄)₃ cationic complexes were structurally characterized by Dias and Krossing.^{4d,e} Cationic gold-ethylene complexes supported by nitrogen ligands have not been structurally characterized.

Complex **9** was synthesized by treating tris(ethylene)-gold hexafluoroantimonate^{4d} with ligand **6** (Scheme 4). It was isolated in 42% yield as a dark red solid. Complex **9** decomposes in solution within an hour at room temperature. Therefore, it is imperative that **9** is prepared at low temperatures to obtain pure material. Solid **9** can be stored at -20 °C under an inert atmosphere for several months. Crystals of **9** suitable for X-ray analysis were grown by layering pentane over the solution of **9** in CH₂Cl₂ at -20 °C. The ORTEP diagram is shown in Figure 4.

The bound ethylene C=C bond length is 1.455(13) Å, which is longer than the values observed for other structurally characterized Au-ethylene complexes at 1.351 to 1.387 Å. However, meaningful comparison of structures is difficult due to the scarcity of well-characterized gold-ethylene complexes.

3. ETHYLENE SELF-EXCHANGE STUDIES

3A. Copper Complex 7b

Ligand exchange in 16-electron complexes usually proceeds by an associative substitution mechanism.¹³ A two-term rate law is often observed: rate = $k_{\text{obs}}[\text{complex}]$, where $k_{\text{obs}} = k_1 + k_2[\text{ligand}]$. The k_1 term arises from associative substitution by solvent, counterion, or impurities. First, the mechanism of ethylene exchange was verified by the dependence of the bound ethylene ¹H NMR line shape on added free C₂H₄. Broadening of the complexed ethylene signal at 3.77–4.01 ppm was observed upon addition of ethylene, showing that ligand exchange is indeed associative.

Second, media-promoted ethylene loss (k_1 term) was analyzed by variable-temperature ¹H NMR spectroscopy. For C₂-symmetric complex **7b**, the k_1 term can be determined by analysis of the complexed C₂H₄ AA'BB' system in the ¹H NMR spectrum that should collapse to a singlet upon media-promoted ethylene loss (followed by rapid reassociation). Thus, media-promoted ethylene loss in **7b** was studied by variable-temperature ¹H NMR in C₂D₂Cl₄. Data were analyzed by line shape analysis of the ethylene region of spectra. First-order rate constants ($k_{1\text{obs}}$, s⁻¹) were obtained by matching observed ¹H NMR spectra with those simulated using the WinDNMR program during coalescence of the bound ethylene

signals.¹⁴ An Eyring analysis¹⁵ of the rate data between 303 and 373 K (see Supporting Information for details) gives $G_{298}^{\ddagger} = 15.9 \pm 0.1$ kcal/mol, $H^{\ddagger} = 9.9 \pm 0.2$ kcal/mol, and $S^{\ddagger} = -20.1 \pm 1.5$ eu. The negative value of the entropy of activation is consistent with associative ligand displacement.¹⁵

Third, ethylene exchange between the bound ethylene of **7b** and free C₂H₄ was studied by variable-temperature ¹H NMR in C₂D₂Cl₄. Ethylene was added to the solution of **7b** via syringe, and the exact quantity of added C₂H₄ (8.8 equiv) was determined by integration of NMR signals. Matching the observed ¹H NMR spectra with those simulated using the WinDNMR program until coalescence of bound and free ethylene signals occurred gave first-order rate constants ($k_{2\text{obs}}$, s⁻¹). An Eyring analysis of the calculated second-order rate data between 256 and 304 K (see Supporting Information for details) gives $G_{298}^{\ddagger} = 12.9 \pm 0.1$ kcal/mol, $H^{\ddagger} = 6.2 \pm 0.5$ kcal/mol, and $S^{\ddagger} = -22.5 \pm 1.7$ eu. As expected, activation parameters are consistent with those expected for associative ligand displacement. The k_1 term for media-promoted ethylene exchange does not provide a significant contribution to k_{obs} since $k_{1\text{obs}} \ll k_{2\text{obs}}$.

3B. Silver Complex 8a

Free and complexed ethylene signals in **8a** are coalesced into a sharp singlet at all temperatures above ca. 156 K. However, at 146 K in CDCl₂F solvent some broadening can be observed as decoalescence appears to be beginning. An approximate upper limit of $G^{\ddagger}$ can be calculated at 146 K using the fast exchange approximation and assuming that the observed broadening of the coalesced signal is due to a slowed exchange rate. The upper limit of $G^{\ddagger}$, assuming associative ligand exchange by analogy with **7b**, was estimated to be ca. 5.0 kcal/mol (see Supporting Information for details). The number is approximate due to the following reasons. First, the equation used for equally populated sites was employed. Second, some broadening of other signals was also observed at 146 K, indicating broadening could be due to other effects. Hence, the calculated $G^{\ddagger}$ value was considered as a higher limit of $G^{\ddagger}$.

3C. Gold Complex 9

Ethylene exchange between **9** and C₂H₄ is slow on the NMR time scale at temperatures up to 50 °C. At those and higher temperatures, complex **9** is unstable and decomposes to colloidal gold. Consequently, the exchange rate could not be determined by NMR line-broadening experiments. Complex **9-d**₄ was prepared in 81% yield by purging a solution of **9** in CH₂Cl₂ with C₂D₄ at -30 °C. ¹H NMR analysis indicated 97% conversion to the labeled complex. An excess of C₂H₄ was added, the exact concentration of C₂H₄ was measured by NMR, and the rate of incorporation of unlabeled ethylene into **9** was monitored by ¹H NMR spectroscopy at 199, 204, 209, and 214 K (Table 1). An Eyring analysis of the rate data (Figure 5) gives $G_{298}^{\ddagger} = 16.7 \pm 0.1$ kcal/mol, $H^{\ddagger} = 10.0 \pm 1.4$ kcal/mol, and $S^{\ddagger} = -22.5 \pm 4.8$ eu. The negative value of the activation entropy is consistent with an associative ligand displacement mechanism.

4. DISCUSSION

We have synthesized and characterized a complete set of group 11 metal complexes possessing the same “sandwich” diimine supporting ligand. Only a few such complete series of coinage metal complexes have been structurally characterized. Krossing and Dias have reported a series of $M(C_2H_4)_3^+X^-$ complexes, where $M = Cu, Ag,$ and Au and $X^- =$ noncoordinating counterion.^{4a–e} Bound ethylene $C=C$ bond lengths vary from 1.33 to 1.36 Å ($M = Cu$) to 1.32–1.33 Å ($M = Ag$) to 1.364 Å ($M = Au$). Dias has disclosed complexes of the general structure $[PhB(3-C_2F_5)Pz)_3]M(C_2H_4)$, where $M = Cu, Ag,$ and Au .^{4f} In this series, $d_{C=C}$ for complexed ethylene is 1.354(7) Å ($M = Cu$), 1.311(5) Å ($M = Ag$), and 1.366(12) Å ($M = Au$). For our series, bound ethylene $C=C$ bond distances are 1.346(8) Å ($M = Cu$), 1.348(10) Å ($M = Ag$), and 1.455(13) Å ($M = Au$). The trend is the same for all three sets, with the greatest complexed ethylene $C=C$ bond lengthening observed for Au and the smallest for Ag and Cu complexes. Results are summarized in Table 2.

Furthermore, we have determined ethylene self-exchange energetics for complexes **7b**, **8a**, and **9**. This study represents the first kinetic study of olefin exchange in isostructural coinage metal complexes. The ethylene self-exchange rate for Ag complex **8a** is too fast to be measured even at 146 K. Estimation of the upper limit of $G^\ddagger$ gives a value of 5.0 kcal/mol. In contrast, the corresponding values for copper and gold complexes **7b** and **9** are $G_{298}^\ddagger = 12.9 \pm 0.1$ kcal/mol, $H^\ddagger = 6.2 \pm 0.5$ kcal/mol, $S^\ddagger = -22.5 \pm 1.7$ kcal/mol (**7b**) and $G_{298}^\ddagger = 16.7 \pm 0.1$ kcal/mol, $H^\ddagger = 10.0 \pm 1.4$ kcal/mol, $S^\ddagger = -22.5 \pm 4.8$ kcal/mol (**9**). The exchange rate shows the following trend: Ag (second transition series) $\gg Cu$ (first transition series) $> Au$ (third transition series).

Inspection of the literature shows several other cases where the ligand exchange rates follow the order 4d metal $>$ 3d metal $>$ 5d metal. Carbon monoxide substitution by phosphine ligands in $CpM(CO)_2$ ($M = Co, Rh, Ir$) systems shows first-order kinetics for both the metal complex and incoming ligand, suggesting an associative substitution mechanism.¹⁶ The substitution rates follow the trend $Rh > Co > Ir$. Interestingly, the tendency observed in $CpM(CO)_2$ and “sandwich” diimine-coinage metal-ethylene complexes is consistent with two studies where dissociative ligand substitution was investigated. Nickel triad $[(EtO)_3P]_4M$ complexes show the fastest exchange for Pd and the slowest for Pt species, with the Ni complex demonstrating an intermediate substitution rate.¹⁷ Further more, substitution reactions of group VI metal hexacarbonyls show the fastest exchange rates for the molybdenum complex.¹⁸ Metal–ligand bond energies in 14-electron $M(C_2H_4)_2^+$ species also follow the trend $Au > Cu > Ag$.¹⁹ Results obtained in our study provide another example of a case where the complex of the second transition series element shows the fastest ligand exchange rates.

5. CONCLUSIONS

We have synthesized and structurally characterized isostructural “sandwich” diimine-coinage metal ethylene complexes. Ethylene self-exchange kinetics in these complexes proceeds by an associative exchange mechanism for Cu and Au complexes. The fastest ligand exchange was observed for Ag complex **8a**, where the exchange rate is too fast to be

accurately measured even at 146 K. Ethylene self-exchange in Cu complex **7b** proceeds with $G_{298}^{\ddagger} = 12.9 \pm 0.1$ kcal/mol, while the exchange is the slowest in Au complex **9**, with $G_{298}^{\ddagger} = 16.7 \pm 0.1$ kcal/mol. Copper complex **7b** is unusually stable and can survive in air for years.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank the Welch Foundation (Chair E-0044) and NIGMS (Grant No. R01GM077635) for supporting this research, and Dr. George N. Oh for collecting diffraction data and solving the X-ray structure of **8b**. Additional X-ray crystallography assistance by Sara N. Vandevelde is gratefully acknowledged. Low-temperature NMR studies of **8a** were performed with the help of Dr. Steven K. Silber, and Prof. Maurice Brookhart is acknowledged for helpful discussions.

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Figure 1.
“Sandwich” Diimine Ligands and Their Palladium Complexes.

Figure 2.

ORTEP view of the molecular structure of **7a**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogens and the triflate counterion are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–C(2) 1.346(8), Cu(1)–C(1) 2.016(5), Cu(1)–C(2) 1.972(5), Cu(1)–N(1) 1.970(4), Cu(1)–N(2) 1.986(4), N(1)–Cu(1)–N(2) 81.94(16).

Figure 3. ORTEP view of the molecular structure of **8b**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogens, CH₂Cl₂, methylcyclohexane, and the tetrafluoroborate counterion are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–C(1) 1.348(10), Ag(1)–C(1) 2.237(4), Ag(1)–N(4) 2.241(3), N(4)–Ag(1)–N(4) 72.46(13).

Figure 4.

ORTEP view of the molecular structure of **9**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogens and the hexafluoroantimonate counterion are omitted for clarity. Selected bond distances (Å) and angles (deg): C(37)–C(38) 1.455(13), Au(1)–C(37) 2.118(8), Au(1)–C(38) 2.094(8), Au(1)–N(1) 2.199(5), Au(1)–N(2) 2.196(5), N(2)–Au(1)–N(1) 73.16(18).

Figure 5.
Eyring plot for ethylene exchange in $9-d_4$.

Scheme 1.
Synthesis of Diimine Ligand 6

Scheme 2.
Synthesis of Copper Complexes **7a** and **7b**

Scheme 3.

Synthesis of Silver Complexes 8a and 8b

Scheme 4.
Synthesis of Gold Complex 9

Table 1
Ethylene Exchange between (Cl₂ArN(CMe))₂Au(C₂D₄)SbF₆ (9-*d*₄) and C₂H₄ in CD₂Cl₂

entry	<i>T</i> (K)	[C ₂ H ₄] (equiv)	[C ₂ H ₄] (M)	<i>k</i> _{obs} (10 ⁻⁴ s ⁻¹)	<i>k</i> _{exh} (10 ⁻⁴ M ⁻¹ s ⁻¹)	activation params ^a
1	199	15.0	0.30	1.38 ± 0.10	4.59 ± 0.6	<i>G</i> ₂₉₈ [‡] = 16.7 ± 0.1
2	204	13.5	0.27	2.59 ± 0.16	9.59 ± 1.1	<i>H</i> [‡] = 10.0 ± 1.4
3	209	7.80	0.16	2.58 ± 0.24	16.3 ± 2.5	<i>S</i> [‡] = -22.5 ± 4.8
4	214	7.90	0.16	4.73 ± 0.48	30.1 ± 4.4	

^a *G*₂₉₈[‡] (kcal/mol), *H*[‡] (kcal/mol), *S*[‡] (eu).

Table 2

Summary of the Properties of Complexes

complex	¹ H NMR δ (C ₂ H ₄), ppm ^a	¹³ C NMR δ (C ₂ H ₄), ppm ^a	¹³ C NMR δ (C ₂ H ₄), ppm ^a	$G_{298}^{\ddagger}$ (kcal/mol)	complex	$d_{O=C}$ (Å)	d_{M-C} (Å)	d_{M-N} (Å)	N–M–N (deg)
7b	4.01–3.93; 3.86–3.77		88.0	12.9 ± 0.1	7a	1.346(8)	1.972(5) 2.016(5)	1.970(4) 1.986(4)	81.94(16)
8a	4.94		105.4	<5.0 ^b	8b	1.348(10)	2.237(4)	2.241(3)	72.46(13)
9	3.31–3.30; 3.28–3.27		65.4	16.7 ± 0.1	9	1.455(13)	2.118(8) 2.094(8)	2.199(5) 2.196(5)	73.16(18)

^a Measured in CD₂Cl₂ for **7b** and in CDCl₃ for **8a** and **9**.^b $G_{146}^{\ddagger}$.