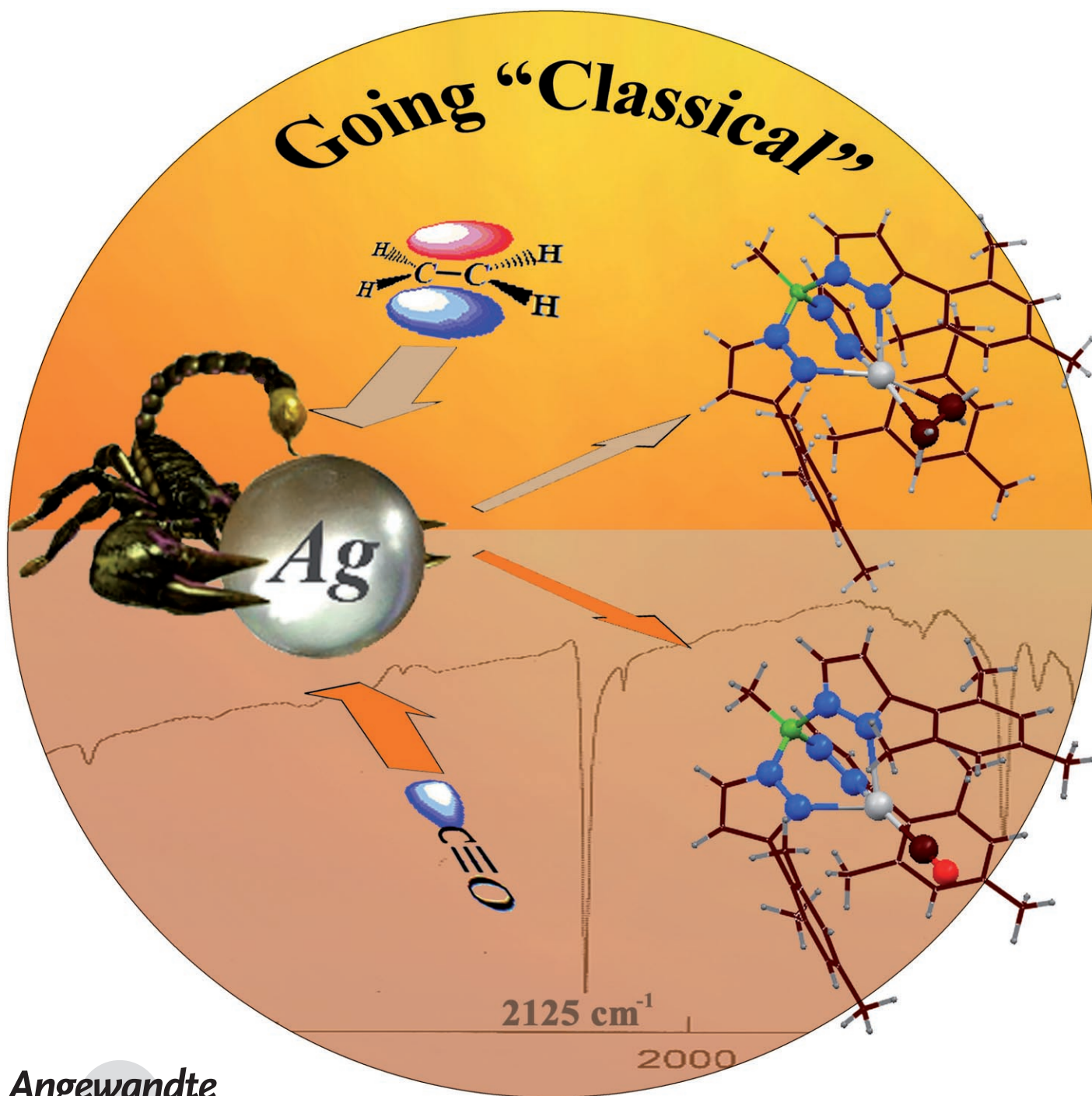


A Classical Silver Carbonyl Complex [$\{\text{MeB}[3\text{-(Mes)pz}]_3\}\text{Ag}(\text{CO})$] and the Related Silver Ethylene Adduct [$\{\text{MeB}[3\text{-(Mes)pz}]_3\}\text{Ag}(\text{C}_2\text{H}_4)\]^*$

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Silver complexes of small unsaturated molecules such as carbon monoxide and ethylene are of tremendous fundamental importance and practical value.^[1–7] Yet, structurally characterized silver(I) complexes featuring CO and C₂H₄ ligands are rare.^[3–12] The isolation of such thermally stable adducts is a very challenging task because silver(I) is a poor σ acceptor, a poor π donor, and in general forms extremely labile adducts with π -acidic ligands.^[1,6] The light sensitivity of silver adducts, the oxidizing nature of silver, and the easy displacement of the coordinated CO and C₂H₄ ligands by many other weakly donating species (which includes common solvents) present further synthetic challenges. The entropic factors arising from “fixing” gases are also believed to play a detrimental role.^[7]

Despite these difficulties, a few Ag^I–CO and Ag^I–C₂H₄ complexes have been isolated and characterized structurally. They include [Ag(CO)₂][B(OTeF₅)₄], [Ag(CO)][B(OTeF₅)₄],^[8,9] [[HB[3,5-(CF₃)₂pz]₃Ag(CO)]],^[10] [[MeB[3-(C₂F₅)pz]₃Ag(CO)]],^[3] [[HB[3,5-(CF₃)₂pz]₃Ag(C₂H₄)],^[11] [[MeB[3-(C₂F₅)pz]₃Ag(C₂H₄)],^[3] [Ag(C₂H₄)][Al{OC(CF₃)₃}₄],^[7] and [HC{(CF₃)C[3,5-(CF₃)₂C₆H₃N]₂}Ag(C₂H₄)] (pz = pyrazolate).^[12] All these compounds contain weakly coordinating, highly fluorinated ligands. Furthermore, silver(I) carbonyl adducts described above exhibit stretching frequencies for ν_{CO} higher than that for free CO (2143 cm^{−1}), and range from 2204 cm^{−1} in [Ag(CO)][B(OTeF₅)₄] to 2153 cm^{−1} in [[MeB[3-(C₂F₅)pz]₃Ag(CO)]]. These are classified as nonclassical metal carbonyl complexes.^[5,13] Herein, we describe the synthesis and structural characterization of the first classical silver carbonyl complex, along with the related silver(I) ethylene adduct. We also demonstrate the successful use of a nonfluorinated, relatively electron-rich ligand in Ag^I–CO and Ag^I–C₂H₄ chemistry.

The complex [[MeB[3-(Mes)pz]₃Ag(C₂H₄)] (**1**, Figure 1) is obtained through a metathesis reaction between the thallium salt [MeB[3-(Mes)pz]₃Tl]^[14] and CF₃SO₃Ag in CH₂Cl₂ under an ethylene atmosphere, and is a white powder with remarkable stability. The ¹H NMR spectroscopic data collected from a week-old sample stored at room temperature in a dark container showed no decomposition.

The X-ray analysis revealed that **1** crystallizes in the R3c space group with a threefold rotation axis containing the B and Ag atoms (Figure 2). The tris(pyrazolyl)borate ligand

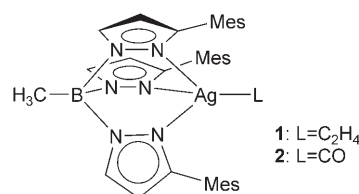


Figure 1. [[MeB[3-(Mes)pz]₃AgL] complexes (L = C₂H₄, CO). Mes = mesityl = 2,4,6-trimethylphenyl.

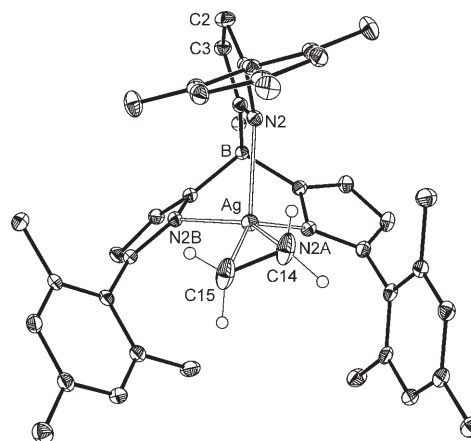


Figure 2. Molecular structure of **1**. All the hydrogen atoms, except those on ethylene moiety, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag–C14 2.27(3), Ag–C15 2.28(3), Ag–N2 2.3404(14), C14–C15 1.323(12), Ag–B 3.422; C14–Ag–C15 33.8(3). Thermal ellipsoids are set at the 35% probability level.

coordinates to the silver ion in a tripodal fashion with an Ag–N bond length of 2.3404(14) Å. The ethylene moiety is distributed equally over three positions inside the coordination pit of the tris(pyrazolyl)borate ligand and coordinates to silver in an η^2 -fashion with a C=C bond length of 1.323(12) Å. The corresponding distance in [[MeB[3-(C₂F₅)pz]₃Ag(C₂H₄)] is not significantly different at 1.314(4) Å.^[3]

The ¹H NMR signal corresponding to the ethylene group appears at δ = 3.42 ppm in the spectrum recorded in CDCl₃, which is significantly upfield compared with the corresponding signal of free ethylene (δ = 5.40 ppm).^[15] The ¹H NMR spectra of related silver ethylene adducts with fluorinated ligands [[HB[3,5-(CF₃)₂pz]₃Ag(C₂H₄)]^[11] and [[MeB[3-(C₂F₅)pz]₃Ag(C₂H₄)]^[3] contain this signal at a relatively downfield region (δ = 5.56 and 5.48 ppm, respectively). The upfield or downfield shifts of these signals resulting from a coordinated ethylene moiety have been previously correlated with an increase or decrease in the ability for M→C₂H₄ π backbonding.^[16] Although greater Ag→C₂H₄ π backbonding is a possibility with **1**,^[17] the relative magnitude of the shift is unusually high and indicates that some additional factors are contributing to the effect. One likely reason for a large upfield shift is the shielding caused by the ring-current effect of the three mesityl substituents that surround the ethylene unit. The ethylene moiety of [HC{(CF₃)C[3,5-(CF₃)₂C₆H₃N]₂}Ag(C₂H₄)]^[12] is somewhat flanked by aryl groups and the signal for the ethylene group is also shifted upfield (δ =

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[**] H.V.R.D. thanks the Robert A. Welch Foundation (grant Y-1289) and the National Science Foundation (CHE-0314666) for financial support of this research. Mes = 2,4,6-trimethylphenyl, pz = pyrazolate. Herein, we use abbreviations based on IUPAC guidelines, that is, ν for frequency and $\tilde{\nu}$ for wavenumber.

Supporting information for this article, including complete details of the synthesis, characterization, and additional X-ray structures, is available on the WWW under <http://www.angewandte.org> or from the author.

3.78 ppm in C_6D_6).^[12] To further investigate this, we synthesized $[MeB[3-(Mes)pz]_3]Cu(C_2H_4)]^{[18]}$ and compared the ethylene signal in the 1H NMR spectrum to that obtained for $[HB[3,5-(Me)_2pz]_3]Cu(C_2H_4)]$ ($\delta = 2.61$ ppm and $\delta = 4.41$ ppm, respectively).^[19] Although the latter has a relatively electron rich copper atom with a greater π -donor capability,^[17] the upfield shift is relatively small compared with the signal for free ethylene ($\delta = 5.40$ ppm). These results are consistent with the possible contribution from ring-current effects, although further studies are required to justify this claim. The shifts in the 1H NMR signals for the ethylene groups in the $[MeB[3-(Mes)pz]_3]M(C_2H_4)]$ adducts ($M = Cu$ and Ag) are in agreement with the greater backbonding ability of copper(I) as compared to silver(I).^[1,5,20]

The ethylene group of **1** is labile in solution; in C_6D_{12} , the 1H NMR spectrum contains a signal at $\delta = 3.40$ ppm which corresponds to the ethylene moiety. Addition of free C_2H_4 to the solution led to the coalescence of the bound ethylene signal. This signal reappeared on purging the solution with N_2 (to remove the excess free ethylene). The ^{13}C NMR signal corresponding to the bound ethylene appears as a broad signal at $\delta = 95.4$ ppm.

Complex **1** is a good precursor to obtain the corresponding Ag^I -CO adduct. The treatment of **1** with carbon monoxide in hexane led to $[MeB[3-(Mes)pz]_3]Ag(CO)]$ (**2**, Figure 1) in quantitative yield. The removal of the solvent under reduced pressure from concentrated solutions of **2** does not lead to the loss of coordinated carbon monoxide but the carbonyl adducts tend to lose carbon monoxide from dilute solutions. However, solid **2** shows remarkable stability; for example, a solid sample of **2** stored in a sealed dark vial (filled with air) at room temperature showed a ν_{CO} band in the IR spectrum even after 60 days.

The FTIR spectrum of **2** in KBr displays a strong band at 2125 cm^{-1} (2128 cm^{-1} in hexane; 2129 cm^{-1} in CH_2Cl_2) that can be assigned to ν_{CO} . This value is lower than that observed for free CO (2143 cm^{-1} , Table 1). As indicated earlier, all the Ag^I -CO compounds that have been structurally characterized thus far show nonclassical behavior ($\tilde{\nu}_{CO} > 2143\text{ cm}^{-1}$).^[5] There is one report that describes the existence of $[CpCo[P(O)(OEt)_2]_3]Ag(CO)]$ with the ν_{CO} band appearing in the classical carbonyl region (2125 cm^{-1} in hexane),^[21] although the ν_{CO} band in methanol appears at 2147 cm^{-1} . In any event, apart from the IR data of the complex in solution, this molecule has not been isolated or fully characterized.

Compound **2** crystallizes in the $P2_1/n$ space group with two chemically similar but crystallographically different molecules in the asymmetric unit. The silver atom adopts a distorted tetrahedral geometry (Figure 3). The average Ag–N bond distance is marginally shorter than those in the ethylene

Table 1: Selected structural and spectroscopic parameters for Au–CO compounds.^[a]

	Compound	$\tilde{\nu}_{CO}$ [cm^{-1}]	Ag–C [Å]	Ag–N [Å] ^[c]	C–O [Å]	Ref.
Nonclassical	$[Ag(CO)][B(OTeF_5)_4]$	2204 ^[b]	2.10(1)		1.077(16)	[22]
	$[Ag(CO)_2][B(OTeF_5)_4]$	2198 ^[b,c]	2.14(5) ^[c]		1.08(6) ^[c]	[22]
	$[Ag(CO)][OTeF_5]$	2189 ^[b]				[22]
	$[HB[3,5-(CF_3)_2pz]_3]Ag(CO)]$	2178 ^[b]	2.037(5)	2.328(4)	1.116(7)	[10]
	$[H_3C[3-(tBu)pz]_3]Ag(CO)]SO_3CF_3$	2154 ^[d]				[23]
	$[MeB[3-(C_2F_5)pz]_3]Ag(CO)]$	2153 ^[e]	2.030(4)	2.314(3)	1.117(4)	[3]
	$[HB[3,4,5-(Br)_3pz]_3]Ag(CO)]$	2153 ^[f]				[24]
	$[HB[3-(CF_3)_5-(Ph)pz]_3]Ag(CO)]$	2149 ^[g]				[17]
	free CO	2143			1.1283	[25]
	$[CpCo[P(O)(OEt)_2]_3]Ag(CO)]$	2125 ^[g] (2147) ^[h]				[21]
Classical	$[MeB[3-(Mes)pz]_3]Ag(CO)]$ (2)	2125 ^[e] 2128 ^[g]	1.994(3) ^[c]	2.305(2)	1.111(4) ^[c]	this study

[a] The presence of a ν_{CO} band in solution is the only evidence for the existence of some of these compounds. Bond distances are given for compounds that have been characterized structurally.

[b] Nujol. [c] Average value. [d] CH_2Cl_2 . [e] KBr. [f] THF. [g] Hexane. [h] MeOH.

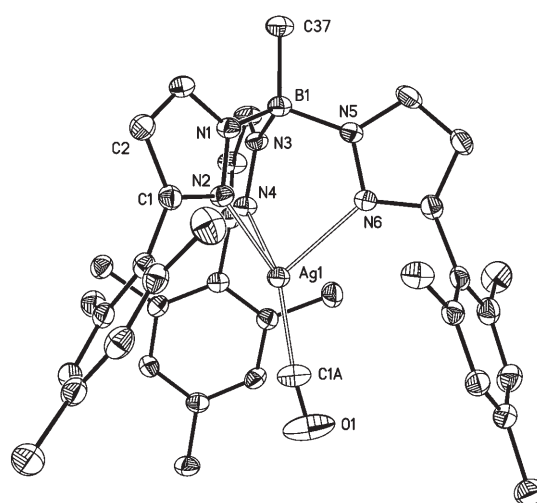


Figure 3. Molecular structure of **2**. All hydrogen atoms and the second molecule in the asymmetric unit have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–C1A 1.995(3), Ag1–N6 2.295(2), Ag1–N4 2.297(2), Ag1–N2 2.316(2), C1A–O1 1.111(4), Ag1...B1 3.393, O1–C1A–Ag1 171.3(4), C1A–Ag1...B1 167.62; (Measurements for the second molecule: Ag2–C2A 1.992(3), Ag2–N8 2.287(2), Ag2–N12 2.312(2), Ag2–N10 2.324(2), C2A–O2 1.112(4), Ag2...B2 3.367, O2–C2A–Ag2 169.2(4), C2A–Ag2...B2 166.25). Thermal ellipsoids are set at the 35% probability level.

adduct **1**. The Ag–C–O moiety is not exactly linear (average angle $170.3(4)^\circ$) and the average Ag–C bond of $1.994(3)$ Å is slightly shorter than those reported for $[MeB[3-(C_2F_5)pz]_3]Ag(CO)]$ and $[HB[3,5-(CF_3)_2pz]_3]Ag(CO)]$ ($2.030(4)$ and $2.037(5)$ Å, respectively). This could be a sign of increased π backbonding in the Ag–CO complex bearing the more electron-rich $[MeB[3-(Mes)pz]_3]^-$ ligand, which is consistent with the observed $\tilde{\nu}_{CO}$ value.^[17]

Preliminary data indicate that it is also possible to prepare the corresponding Cu^I and Au^I adducts.^[18] The ν_{CO} band of $[MeB[3-(Mes)pz]_3]Cu(CO)]$ appears in the IR spectrum at 2075 cm^{-1} (KBr) whereas for $[MeB[3-(Mes)pz]_3]Au(CO)]$, this band appears at 2083 cm^{-1} (hexane). This group trend of

$\tilde{\nu}_{\text{CO}}(\text{Cu}) < \tilde{\nu}_{\text{CO}}(\text{Au}) < \tilde{\nu}_{\text{CO}}(\text{Ag})$ is in excellent agreement with both theoretical and experimental data already reported in the literature,^[5,20] and clearly shows that the $\text{M} \rightarrow \text{L} \pi$ back donation decreases from Cu^{I} to Ag^{I} and increases again from Ag^{I} to Au^{I} .

In conclusion, we have shown that it is possible to synthesize and isolate thermally stable $\text{Ag}-\text{CO}$ and $\text{Ag}-\text{C}_2\text{H}_4$ adducts using a nonfluorinated, electron-rich ligand $[\text{MeB}\{3-(\text{Mes})\text{pz}\}_3]^-$, and compound **2** is the first structurally characterized classical silver carbonyl complex.

Experimental Section

1: ^1H NMR (CDCl_3 , 298 K): δ = 1.13 (s, 3H, BCH_3), 1.86 (s, 18H, $o\text{-CH}_3$), 2.21 (s, 9H, $p\text{-CH}_3$), 3.42 (s, 4H, $\text{CH}_2=\text{CH}_2$), 6.00 (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C4H), 6.77 (s, 6H, $m\text{-CH}$), 7.78 ppm (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C5H); ^1H NMR (C_6D_{12} , 298 K): δ = 1.13 (s, 3H, BCH_3), 1.86 (s, 18H, $o\text{-CH}_3$), 2.18 (s, 9H, $p\text{-CH}_3$), 3.40 (s, 4H, $\text{CH}_2=\text{CH}_2$), 5.89 (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C4H), 6.69 (s, 6H, $m\text{-CH}$), 7.72 ppm (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ = 5.0 (br s, BCH_3), 20.6, 21.1, 95.4 (br s, $\text{CH}_2=\text{CH}_2$), 103.6, 127.7, 132.9, 133.1, 137.1, 138.0, 150.3. Crystal data for **1**: $\text{C}_{39}\text{H}_{46}\text{N}_6\text{AgB}$, rhombohedral, $R3c$; 100 K; $a = b = 12.0079(5)$, $c = 43.861(2)$ Å, $V = 5477.0(4)$ Å³, $Z = 6$; $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0176, $wR2 = 0.0452$.

2: FTIR: $\tilde{\nu}_{\text{CO}} = 2125 \text{ cm}^{-1}$ (KBr pellets, the ^{13}CO satellite was observed at 2079 cm^{-1} , resolution 1 cm^{-1}); 2128 cm^{-1} (hexane, resolution 2 cm^{-1}); 2126 cm^{-1} (nujol, resolution 2 cm^{-1}); 2129 cm^{-1} (CH_2Cl_2 , resolution 2 cm^{-1}); ^1H NMR (C_6D_{12} , 298 K): δ = 1.11 (s, 3H, BCH_3), 1.86 (s, 18H, $o\text{-CH}_3$), 2.15 (s, 9H, $p\text{-CH}_3$), 5.91 (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C4H), 6.69 (s, 6H, $m\text{-CH}$), 7.70 ppm (d, 3H, $^3J_{\text{HH}} = 2.0$ Hz, C5H). Crystal data for **2**: $\text{C}_{38}\text{H}_{42}\text{N}_6\text{AgBO}$, monoclinic, $P2_1/n$; 198 K; $a = 24.2090(17)$, $b = 11.2923(8)$, $c = 26.8553(19)$ Å; $\beta = 100.8030(10)^\circ$, $V = 7211.5(9)$ Å³, $Z = 8$; $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0402, $wR2 = 0.0907$.

1 from **2**: Ethylene was bubbled through a solution of **2** in hexane at room temperature to give the corresponding ethylene adduct in quantitative yield.

CCDC-622971 and CCDC-622972 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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