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New chromium, molybdenum, and cobalt complexes of the chelating esp ligand

Ryan J. Pakula, Andrea M. Martinez, Efrey A. Noten, Caleb F. Harris, John F. Berry

Department of Chemistry, University of Wisconsin – Madison, 1101 University Ave., Madison, WI 53706, United States

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ABSTRACT

Bimetallic carboxylates of Rh(II) are widely recognized for their ability to catalyze carbene transfer reactions such as the cyclopropanation of olefins using organic diazo compounds as carbene precursors. A major goal in catalysis is to find cheaper, more Earth-abundant alternatives to precious metal catalysts. There is therefore currently great interest in the bimetallic paddlewheel chemistry of elements that have lower costs and greater terrestrial abundance than Rh. M₂(esp)₂(L)₂ structures were synthesized and structurally characterized with M = Cr, Co, and Mo, where $esp^{2-} = \alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionate, a chelating di-carboxylate ligand that helps stabilize the bimetallic core. Cr₂(esp)₂(THF)₂, Mo₂(esp)₂, and Co₂(esp)₂(EtOH)₂ were tested as catalysts for decomposition of the diazo compound (4-bromophenyl)diazoacetate methyl ester in the presence of styrene; while the Cr2 and Mo2 complexes showed no difference from a background control, the Co2 complex was found to enhance the rate of dinitrogen extrusion, and promote carbene addition to styrene to form the cyclopropane product. © 2019 Elsevier Ltd. All rights reserved.

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1. Introduction 33

34 Bimetallic coordination complexes adopting the paddlewheel structure are found throughout the transition series and support 35 36 a range of metal-metal interactions, from strong multiple bonds to weaker antiferromagnetically coupled systems. Singly-bonded 37 Rh⁴⁺ complexes are perhaps the most well-known and have found 38 widespread use in catalyzing carbene and nitrene transfer reac-39 tions [1]. Metal-metal bonded Ru₂⁵⁺ catalysts are known in oxida-40 tion chemistry [2] and intramolecular C-H amination [3], and 41 singly-bonded Pd₂⁶⁺ structures are implicated as catalytic interme-42 diates [4]. To these examples are being added a number of new 43 metal-metal bonded catalysts for a variety of important transfor-44 45 mations [5], and novel catalyst discovery continues to be an important area of research for metal-metal bonded compounds. Because 46 the most well-established examples are based on Rh, Ru, and Pd, 47 which are all relatively expensive, rare, and toxic as compared with 48 49 many other metals known to form analogous bimetallic structures, a major goal in catalyst discovery is to explore complexes with 50 Earth-abundant elements [6]. We therefore initiated studies to tar-51 52 get the preparation of new examples of tetragonal, paddlewheeltype structures containing these elements. Our initial efforts were 53 to explore Rh-Bi structures, which perform similar chemistry to 54 55 Rh₂ complexes but contain half the number of precious metal

atoms [7]. Here, we explore complexes that contain only base metals: Cr, Mo, and Co. In order to stabilize first row transition metal bimetallic structures, we focused our efforts on use of the chelating dicarboxylate ligand esp (esp²⁻ = $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionate). This ligand (named after the first author of the initial report) was found to be critical in enabling intermolecular C-H amination chemistry using Rh₂ complexes [8], and it has been shown to be useful in accessing more stable and typically more soluble complexes than monodentate carboxylates [7b,9]. The stability of esp-supported coordination compounds has been attributed to the chelate effect, which we hypothesized would be helpful for supporting complexes of the relatively labile first-row transition metals. We recently reported that the esp ligand could be used to stabi-

lize a paddlewheel-type Co_2^{4+} complex, $Co_2(esp)_2(EtOH)_2$ [10]. In this report, we describe a number of further small molecule adducts of the $Co_2(esp)_2$ core. These adducts are remarkable in that, prior to this study, discrete Co₂(O₂CR)₄ structures have only been known to be stabilized by having nitrogen heterocycles as axial ligands [11]. Here, we find that a greater variety of small axial ligands, namely EtOH, CH₃CN, and H₂O, can yield stable axial adducts and that simple axial ligand substitution chemistry can occur at the Co_2^{4+} core, an important requisite elementary step for catalysis. We also report conditions that lead to the loss of the Co₂ paddlewheel-type structure, and preliminary efforts at using $Co_2(esp)_2(EtOH)_2$ as a catalyst for the cyclopropanation of styrene.

E-mail address: berry@chem.wisc.edu (J.F. Berry).

* Corresponding author.

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82 2. Experimental

83 2.1. Materials

84 All compounds were obtained from commercial sources and used as received, except as noted. All work was performed with 85 86 oven-dried glassware under a dry, nitrogen atmosphere using stan-87 dard Schlenk techniques or an inert-atmosphere glovebox, except 88 as noted. Anhydrous CoCl₂ was desiccated by heating CoCl₂ from 89 Strem to reflux in SOCl₂, followed by rinsing with anhydrous hex-90 anes to remove all traces of SOCl₂. $Cr_2(OAc)_4(H_2O)_2$ was synthe-91 sized according to known methods [12], starting from 92 commercial CrCl₃·6 H₂O. Flash chromatography was performed using SiliCycle SiliaFlash P60 silica gel (40–63 µm/230–400 mesh) 93 in the indicated solvents. 94

95 For air-free manipulations, solvents were dried and de-oxy-96 genated in the following ways: tetrahydrofuran (THF), toluene, 97 and hexanes were dried using a VAC solvent system and sparged 98 with nitrogen prior to use. Dichloromethane and butyronitrile 99 (PrCN) were dried over CaH₂ and distilled under nitrogen immedi-100 ately prior to use. Ethanol was dried over Mg(OEt)₂ and distilled 101 under nitrogen immediately prior to use.

102 The H₂esp ligand was synthesized as reported in the literature 103 [8,10]. $Co_2(esp)_2(EtOH)_2$ was prepared as previously described 104 [10].

105 2.2. Preparation of Cr and Mo complexes

106 2.2.1. Cr₂(esp)₂(PrCN)₂ (1·2PrCN)

Cr₂(OAc)₄(H₂O)₂ (188 mg, 0.500 mmol) was placed in a 50 mL 107 108 Schlenk flask with a stirbar and heated at 100 °C under vacuum 109 for 1.5 h to remove the axial water ligands, yielding a brown powder. Freshly distilled butyronitrile (20 mL) was added, and the mix-110 ture was heated to reflux at 100-120 °C for 30 min then allowed to 111 112 cool to room temperature, yielding a red/brown suspension. In a 113 separate Schlenk flask, H2esp (280 mg, 1.01 mmol) and butyroni-114 trile (15 mL) were combined and heated gently with swirling until 115 the H₂esp dissolved. The colorless H₂esp solution was transferred 116 via cannula into the flask containing the $Cr_2(OAc)_4$. The reaction 117 mixture was then heated, and the red solids quickly dissolved. 118 After about 5 min, the reaction mixture was allowed to cool to 119 room temperature. Cooling the mixture to -80 °C yielded large, 120 orange, air-sensitive, plate-shaped crystals. The yield of analyti-121 cally pure product was too poor for further characterization.

2.2.2. Cr₂(esp)₂(THF)₂ (1.2THF) 122

Cr₂(OAc)₄(H₂O)₂ (266 mg, 0.707 mmol) was placed in a Schlenk 123 124 flask with a stirbar and heated at 110 °C under vacuum to remove 125 the axial water ligands, yielding a brown powder. Dry, deoxy-126 genated THF (40 mL) was added to solid H₂esp (416 mg, 1.50 mmol), and the resulting solution was transferred via cannula 127 128 into the flask containing the $Cr_2(OAc)_4$. The reaction mixture was heated to reflux for 10 min then cooled to room temperature. 129 130 The volatiles were removed in vacuo, diethyl ether (70 mL) was added, and the mixture was filtered. After removal of the ether, 131 132 the product was obtained as a red/orange powder in quantitative yield. Solvent diffusion of pentane into a toluene solution of the 133 134 complex at room temperature afforded large, brown, air-sensitive, 135 block-shaped crystals over 2 days suitable for single crystal X-ray 136 analysis. Anal. Calc. for C₄₀H₅₆Cr₂O₁₀·H₂O: C, 58.67; H, 7.14. Found: 137 C, 58.43; H, 6.99. ¹H NMR (500 MHz; CDCl₃) δ : 7.10 (br s, 2H), 6.96 138 (t, J = 6.6 Hz, 2H), 6.76 (d, J = 6.6 Hz, 4H), 4.05 (s, 8H), 2.61 (s, 8H), 1.89 (s, 8H), 0.95 (s, 24H). ¹³C NMR (125 MHz; CDCl₃) δ: 137.4, 139 140 130.2, 127.3, 126.7, 125.5, 68.5, 46.7, 45.8, 42.0, 25.3, 24.6. FTIR 141 (ATR, cm^{-1}) : 2964(w), 2924(w), 2876(w), 1578(m), 1559(m),

1476(m), 1420(m), 1362(w), 1262(m), 1092(m), 1021(m), 870 142 (w), 799(s), 749(w), 708(m), 621(s). $C_{32}H_{40}Cr_2O_8$ [M]⁺: 656.2, 143 found: 656.1. 144

2.2.3. $[Cr_2(esp)_2(H_2esp)]_n$ (**1**·H₂esp)

In air, hydrochloric acid (10 mL, 1 M aqueous solution) was added to orange HgO (30.7 mg, 0.140 mmol) in a Schlenk flask and stirred for 15 min, yielding a colorless solution. With slow stirring, zinc powder (330 mg, 5.00 mmol) was added slowly to give light grey pebbles of Zn amalgam. The mixture was stirred for 15 min before the supernatant was decanted off and the amalgam then rinsed with 3×10 mL of water to remove the ZnCl₂ byproduct. The solid Zn amalgam was then dried under vacuum.

Deoxygenated water (30 mL) was transferred via cannula into a Schlenk flask containing CrCl₃·6H₂O (73.6 mg, 0.280 mmol) to give 155 a green solution. This Cr³⁺ (aq) solution was then transferred via 156 cannula to a flask containing Zn/Hg, and the resulting mixture 157 was stirred for one hour to yield a light blue Cr^{2+} (aq) solution. In 158 a separate flask, H₂esp (108 mg, 0.390 mmol) was dissolved in 159 deoxygenated ethanol (10 mL), and the Cr²⁺ (aq) solution was 160 added to the H₂esp solution via cannula. The flask was outfitted 161 with a reflux condenser and the pink suspension was heated to 162 reflux at 85 °C for 3 h, cooled to room temperature, and filtered 163 and the filtrate was discarded. The red solid was dissolved in 164 toluene, and single crystals of red $[Cr_2(esp)_2(H_2esp)]_n C_7H_8$ were 165 obtained by vapor diffusion of hexanes into the toluene solution. Yield: 20.0 mg, 8.1%. MS (MALDI-TOF) m/z calcd for $C_{32}H_{40}Cr_2O_8$ [M]⁺: 656.2, found: 656.1.

2.2.4. Mo₂(esp)₂ (2)

 $Mo_2(OAc)_4$ (500 mg, 1.20 mmol) and H_2esp (720 mg, 170 2.60 mmol) were combined in a 50 mL Schlenk flask with a stirbar. 171 The flask was evacuated and backfilled with nitrogen three times, 172 then outfitted with a septum. Freshly distilled, deoxygenated EtOH 173 (25 mL) was added, and the reaction mixture was heated to reflux 174 at 90 °C for 1 h. After cooling to room temperature, the reaction 175 mixture was stirred at room temperature for 2 days. The reaction 176 mixture remained yellow the entire time; though, when stirring 177 was ceased, a yellow solid settled below a brown mother liquor. 178 The solids were collected via filtration, rinsing with 3×10 mL 179 EtOH followed by 2×10 mL diethyl ether. The yellow solid was 180 dried in vacuo for 3 days. Yield: 673 mg, 77%. Anal. Calc. for C₃₂H₄₀-181 Mo₂O₈: C, 51.62; H, 5.42. Found: C, 52.08; H, 5.26. ¹H NMR 182 (400 MHz; DMSO- d_6) δ : 7.19 (t, J = 7.4 Hz, 2H), 7.13 (t, J = 1.1 Hz, 183 2H), 7.04 (dd, J = 7.4, 1.1 Hz, 4H), 2.96 (s, 8H), 1.38 (s, 24H). ¹³C 184 NMR (100 MHz; DMSO-d₆) δ : 186.2, 138.1, 130.6, 128.1, 126.9, 185 47.5, 45.4, 26.4. FTIR (ATR, cm⁻¹): 2987(w), 2967(w), 2920(w), 186 2865(w), 1508(s), 1472(m), 1445(m), 1413(s), 1376(m), 1358(m), 187 1261(m), 1244(m), 903(m), 882(m), 825(m), 773(m), 747(m), 705 188 (s), 615(s). MS (MALDI-TOF) m/z calcd for $C_{32}H_{40}Mo_2O_8$ [M]⁺: 189 746.1, found: 746.0. 190

2.3. Crystallization of $Co_2(esp)_2$ solvent adducts

2.3.1. Co₂(esp)₂(CH₃CN)₂ (3·2CH₃CN)

Crystals of Co₂(esp)₂(EtOH)₂ were soaked in MeCN in air for 193 2 days. Purple crystals of Co₂(esp)₂(CH₃CN)₂ were obtained that 194 appear cyan/olive dichroic under polarized light. 195

2.3.2. $Co_2(esp)_2(H_2O)_2$ (3.2 H_2O)

Crystals were obtained by layering a CH₂Cl₂ solution of Co₂(-197 $esp)_2(EtOH)_2$ with a layer of diethyl ether in air. After several days, 198 blue crystals were obtained that are yellow/purple dichroic under 199 polarized light. 200

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201 2.3.3. $[Co_2(esp)_2(MeOH)_2]_n$ (4)

202 Purple needle-shaped crystals grew via slow evaporation of a 203 CH_3OH solution of $Co_2(esp)_2(EtOH)_2$ in air.

2.3.4. $Co_2(esp)_2(py)_4(H_2O)$ (5) 204

Red block-shaped crystals grew via slow evaporation of a pyri-205 206 dine solution of Co₂(esp)₂(EtOH)₂ in air.

207 2.3.5. $[Co_2(esp)_2]_n$ (**6**)

Co₂(esp)₂(EtOH)₂ was dissolved in a mixture of CH₂Cl₂ and Et₂O, 208 209 and the resulting solution was allowed to evaporate in air, yielding 210 crystals of the coordination polymer $[Co_2(esp)_2]_n$.

211 2.4. Other attempts to prepare $Co_2(esp)_2$

212 2.4.1. $[CoLi_{10}(esp)_6(H_2O)_2(MeCN)]_n \cdot 5 MeCN (7)$

213 H₂esp (122 mg, 0.438 mmol) was placed in an oven-dried Schlenk flask with a stirbar, and vacuum dried for several hours. A 214 215 minimal amount of anhydrous, deoxygenated THF was added to 216 yield a solution, ca. 2 mL, and the solution was cooled to -78 °C in a dry ice/acetone bath. "BuLi (300 µL of 2.5 M solution in hex-217 anes, 0.750 mmol) was added slowly, and the resulting solution 218 219 was stirred for 3 h, slowly warming to room temperature. Anhydrous CoCl₂ (50.0 mg, 0.400 mmol) was placed into a 10 mL Sch-220 lenk flask and THF (10 mL) was added to yield an intense 221 cerulean suspension. The suspension was sonicated for 5 min to 222 help solubilize the salt. The Co²⁺ suspension was then transferred 223 via cannula into the flask containing the Li₂esp solution. The result-224 225 ing mixture briefly turned vellow followed by a persistent dark blue/teal color. After stirring for 3 h, the resulting suspension 226 was filtered under nitrogen to remove a white solid. Residual 227 THF was removed from the filtrate *in vacuo* to yield a purple solid. 228 229 The purple solid was dissolved in toluene and precipitated by addi-230 tion of hexanes to yield a pink solid. The pink solid was then dis-231 solved in MeCN in air to yield a blue solution, which yielded 232 purple plate-shaped crystals upon slow evaporation.

2.4.2. [Co(esp)(H₂O)₃]_n·2 H₂O (**8**) 233

234 In air, an Erlenmeyer flask was loaded with H₂esp (100 mg, 0.360 mmol), Ba(OH)₂·8 H₂O (90.0 mg, 0.300 mmol), 20 mL H₂O, 235 236 and a stirbar. The mixture was stirred at room temperature for 237 5 min, followed by addition of CoSO₄·7 H₂O (110 mg, 0.390 mmol). 238 The solution immediately turned pink and almost all of the solid 239 dissolved briefly, and then a white solid (presumably $BaSO_4$) began 240 to precipitate. MeCN (20 mL) was added, and the reaction mixture 241 was heated to reflux for 15 min then filtered hot through filter paper to remove the solids. The pink filtrate was concentrated to 242 243 dryness, exposed to vacuum - upon which the purple residue 244 turned pink - and was dissolved in CH₂Cl₂. Slow evaporation of 245 the CH₂Cl₂ solution yielded pink plate-shaped crystals that are 246 blue/yellow dichroic under polarized light.

247 2.5. Reactions with diazo compounds

248 2.5.1. Monitoring decomposition of methyl (4-methoxyphenyl)diazoacetate 249

Reaction progress was monitored by in situ IR spectroscopy 250 using a Mettler Toledo ReactIR ic10 with an AgX probe. The data 251 collection window was centered on the diazo stretch of methyl 252 (4-methoxyphenyl)diazoacetate at 2085 cm⁻¹. Time points were 253 taken every 15 minutes, with 32 scans per timepoint. The experi-254 255 ment was conducted using either $Cr_2(esp)_2(THF)_2$ or $Co_2(esp)_2(-$ 256 EtOH)₂ as a catalyst, and additionally a control experiment was 257 performed without any catalyst.

For each experiment, the respective $M_2(esp)_2$ complex (0.010 mmol, 10 mol%), styrene (120 µL, 10.7 eq.), and 1,2-dichloroethane (DCE) (5 mL) were loaded into a 3-neck Schlenk flask with a stirbar, and the flask was evacuated and backfilled with nitrogen. The reaction mixture was heated to 50 °C, and the ReactIR dip probe with a Teflon adapter was inserted and background scans were collected. A solution of 20.0 mg (4-methoxyphenyl)diazoacetate methyl ester in 300 µL DCE was added, using an additional 700 µL DCE to ensure full transfer. The reaction was monitored for 24 h (Scheme 1).

2.5.2. Cyclopropanation of styrene with methyl (4-bromophenyl)diazoacetate

This experiment was conducted using either $Cr_2(esp)_2(THF)_2$, 270 $Mo_2(esp)_2$, or $Co_2(esp)_2(EtOH)_2$ as a catalyst, and additionally a 271 control experiment was performed without any catalyst. The 272 $M_2(esp)_2$ complex (0.010 mmol, 10 mol%), styrene (120 μ L, 273 10.7 eq.). methvl (4-bromophenyl)diazoacetate (25.5 mg) 274 0.100 mmol) and 1,2-dichloroethane (DCE) (5 mL) were loaded 275 into a septum-capped vial under nitrogen. The reaction mixtures 276 were heated to 50 °C for 16 h and the volatiles were removed under high vacuum. The control as well as the reaction mixtures containing Mo₂(esp)₂ and Cr₂(esp)₂(THF)₂ were reconstituted in CDCl₃ and subjected to ¹H NMR spectroscopy. The reaction catalyzed by Co₂(esp)₂(EtOH)₂ was dissolved in CH₂Cl₂ and passed through a $1 \text{ cm} \times 1 \text{ cm}$ plug of silica gel to remove paramagnetic impurities before subjecting to ¹H NMR spectroscopy. The yields of cyclopropanated product using $Cr_2(esp)_2(THF)_2$ or $Mo_2(esp)_2$ did not vary significantly from the control (<5% conversion), however the reaction performed in the presence of $Co_2(esp)_2(EtOH)_2$ provided the cyclopropanated product in 71% spectroscopic yield. The product was isolated by silica gel column chromatography in 49% yield using a 2.5 cm diameter column packed 12 cm high with silica. A combination of hexanes and ethyl acetate (1:0-8:1) were 291 used as the eluent, changing from neat hexanes to the more polar combination after the less polar impurity had eluted from the column. The ¹H NMR spectrum matched that previously reported [13]. ¹H NMR (400 MHz; CDCl₃) δ: 7.26–7.24 (m, 2H), 7.10–7.08 (m, 3H), 6.90-6.88 (m, 2H), 6.79-6.76 (m, 2H), 3.66 (s, 3H), 3.11 (dd, J = 9.4, 7.3 Hz, 1H), 2.14 (dd, J = 9.4, 5.0 Hz, 1H), 1.84 (dd, *I* = 7.3, 5.0 Hz, 1H).

2.6. Instrumentation and general notes

NMR spectroscopy and mass spectrometry experiments were 299 performed in the Paul Bender Chemical Instrumentation Center 300 in the Chemistry Department at the University of Wisconsin-Madi-301 son. NMR spectra were recorded on both Bruker Avance 400 MHz 302 (¹H; 100 MHz for ¹³C) and 500 MHz (¹H; 125 MHz for ¹³C) spec-303 trometers, and a cryoprobe was used for obtaining routine spectra 304 at +24.0 °C. ¹H chemical shifts are reported on a ppm scale refer-305 enced to tetramethylsilane (TMS) at 0 ppm; ¹³C NMR spectra were 306 collected with decoupling from ¹H and referenced to residual sol-307 vent signal. Mass spectral data were collected using a Thermo Q 308 Exactive Plus ESI mass spectrometer or using an anthracene matrix 309 on a Bruker ULTRAFLEX III MALDI-TOF mass spectrometer 310



Scheme 1.

Table 1

Crystallographic data for 1 2PrCN and 1 H₂esp.

Compound	1 2PrCN	1-2THF	1 ⋅ H ₂ esp ⋅ toluene
Formula	C ₄₀ H ₅₄ Cr ₂ N ₂ O ₈	C ₄₀ H ₅₆ Cr ₂ O ₁₀	C ₅₅ H ₇₀ Cr ₂ O ₁₂
Formula weight	794.85	800.87	1027.11
Crystal system	monoclinic	triclinic	triclinic
Space group	P2/n	$P\overline{1}$	$P\overline{1}$
T (K)	100	100	100
a (Å)	19.9901(5)	9.621(3)	12.3040(3)
D (A) c (Å) α (°)	20.1501(5) 90	10.686(3) 11.245(4) 76.087(15)	12.4295(3) 19.6911(4) 88.007(1)
β(°)	94.397(2)	67.503(9)	72.333(1)
γ(°)	90	68.601(7)	67.160(1)
$V(\dot{A}^3)$	4037.3(2)	987.7(5)	2632.6(1)
	4	1	2
$ ho_{ m calc}~(m mg~mm^{-3})\ \mu~(m mm^{-1})$	1.308	1.346	1.296
	0.590	0.605	0.473
F(0 0 0)	1680	424	1088
λ (Å)	0.71073	0.71073	0.71073
R_{int} $R_1 (I > 2\sigma(I))$ $R_1 (a I data)$	0.0998 0.0468	0.0330 0.0304	0.0279 0.0328
wR_2 (I > $2\sigma(I)$) wR_2 (all data)	0.0952 0.0920 0.1093	0.0737 0.0765	0.0415 0.0850 0.0902

$${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$$

^bwR₂=
$$\sqrt{\sum \left[w\left(F_o^2 - F_c^2\right)^2\right] / \sum \left[w\left(F_o^2\right)^2\right]}; w = \frac{1}{\left[\sigma^2(F_o^2) + (aP)^2 + bP\right]};$$

 $P = \left[\max\left(\mathsf{Oor}F_o^2\right) + 2F_c^2\right]/3.$

311 equipped with a SmartBeam laser. IR spectra were collected on a 312 Bruker Tensor 27 FTIR spectrometer using the ATR technique. Ele-313 mental analyses were measured at Midwest Microlab, LLC in Indi-314 anapolis, Indiana, USA.

315 2.7. Crystallography

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316 Crystallographic data were measured at the Molecular Structure 317 Laboratory of the Chemistry Department of the University of Wis-318 consin - Madison. Crystals were selected under oil under ambient 319 conditions and attached to the tip of a MiTeGen MicroMount. Each crystal was mounted in a stream of cold nitrogen at 100(1) K and 320 321 centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar 322 323 SMART APEX-II diffractometer with either Mo K α (λ = 0.71073 Å) 324 radiation or Cu K α (λ = 1.54178 Å) radiation. The data were col-325 lected using a routine to survey an entire sphere of reciprocal space 326 and indexed by the SMART program [14]. The structures were solved, 327 using the OLEX2 program [15], via direct methods or charge flipping 328 and refined by iterative cycles of least-squares refinement on F^2 329 followed by difference Fourier synthesis [16]. All H atoms were 330 included in the final structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative 331 332 isotropic displacement coefficients, except as noted. Crystallo-333 graphic data for the Cr-containing structures are summarized in 334 Table 1, and the data for the Co complexes are given in Table 2. 335

For all twinned structures, all possible combinations of domains and inclusion or exclusion of overlapping reflections were used to generate HKLF5 files. The HKLF4 or HKLF5 file which yielded the smallest uncertainties in bond distances was used for the final refinement.

During refinement of 4, both MeOH O–H bonds were treated in the following ways: the O–H distances were restrained to 0.87 Å using the DFIX command, and DANG was used on the C...H and Co...H distances to restrain the orientation of the O-H bond.

The crystal structure of **5** contains two Co₂ units, one of which with a disordered esp ligand. The two disordered parts differ in the

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orientation of the esp phenylene ring; the two disordered phenyl 346 rings are offset from each other by 41°, with a 60:40 ratio of the 347 two positions. The EADP constraint was used to obtain a reason-348 able refinement on carbon atoms C70, C71, C72, and C73; the cor-349 responding carbon atoms in the minor component were refined 350 isotropically. 351

During refinement of 7, the model was treated with the SQUEEZE function [17] of the PLATON program [18] to remove severely disordered solvent molecules from the structure. This procedure removed 45 electrons from a space of 396 Å³, which is consistent with 2 MeCN molecules per unit cell, or one per CoLi10 repeating unit (in addition to the four interstitial MeCN molecules that were modeled). The data were only of high quality to a resolution of 0.88 Å.

During refinement of **8**, we found three bound water molecules per cobalt center (each of which resides on a crystallographic inversion center) and two additional water molecules in the lattice that are hydrogen bonded to the Co/esp framework. In order to reach a stable refinement, a same-distance restraint (SADI) was applied to the disordered carbonyl C-O bond (C16-O4/O4A), a fixed-distance restraint (DFIX) was used for the O-H distances of the O5 water molecule, and the other water molecules were treated with AFIX 6 (08 and 09; hydrogen-bonded solvates) or AFIX 7 (O6 and O7; Co-bound).

3. Results and discussion

3.1. Overview of Cr, Mo, and Co carboxylate chemistry

Since the report of Du Bois and coworkers in using the esp 372 ligand to improve Rh₂ catalyst systems [8], many other esp-stabi-373 lized structures have been reported, including with Ru₂ [3,19], 374 Re₂ [9a], Pd₃ [20], Co₂ [10], Cu₂ [9b], and heterobimetallic Bi-Rh 375 cores [7b]. To date, only the μ_2 -RCOO- $\kappa^1(O)$, $\kappa^1(O')$ coordination 376 mode with both carboxylate groups has been observed with esp 377 (as seen in Fig. 1A), which is noteworthy because carboxylate 378 ligands can in general display a number of other coordination 379 modes such as κ^1 , κ^2 , bridging or non-bridging, etc. [21]. That said, 380 the metals in the complexes with which the coordination chem-381 istry of esp has been explored all show a distinct preference for 382 the μ_2 -RCOO- $\kappa^1(0), \kappa^1(0')$ coordination mode [6]. Cr and Mo are 383 two further examples of metals for which the bridging bidentate 384 coordination mode of carboxylate ligands is well-known to yield 385 paddlewheel-type bimetallic structures with metal-metal bonds. 386 Indeed, we report here that paddlewheel-type structures for these 387 metals are supported by the esp ligand. For Co(II), however, car-388 boxylate ligands can adopt a variety of coordination modes. The 389 distribution of the coordination modes found for acetate com-390 plexes in the Cambridge Structural Database (CSD) is shown in 391 Fig. 1. While the desired bridging bidentate mode is found in the 392 majority of the complexes known, 45% of the structures contain 393 acetates in some other coordination mode. Consistent with this 394 structural diversity, and the fact that the esp ligand contains two 395 separate carboxylate binding sites, our investigations with Co 396 reveal a more diverse carboxylate coordination chemistry of esp. 397

3.2. Chromium and molybdenum complexes of esp

Complexes with Cr₂ and Mo₂ cores supported by the esp ligand 399 were of particular interest due to the strong metal-metal bonding 400 in these systems [6], a feature believed to be critical to the efficacy 401 of Rh₂ systems at performing carbene and nitrene transfer 402 reactions [22]. Additionally, Cr₂ complexes are highly Lewis acidic, 403 similar to Rh₂ systems. For example, both systems will coordinate 404 weak σ -donor ligands, as in the case of $[Cr_2(O_2CCPh_3)_4(\eta^6-C_6H_6)]_n$ 405

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Table 2

Crystallographic data for 3·2CH₃CN, 3·2H₂O, 4, 5, 7, and 8.

Compound	3 2CH ₃ CN	3-2H ₂ 0	4	5	7	8
Formula	C ₃₆ H ₄₆ Co ₂ N ₂ O ₈	C ₃₂ H ₄₄ Co ₂ O ₁₀	C ₃₄ H ₄₈ Co ₂ O ₁₀	C ₁₀₄ H ₁₂₄ C0 ₄ N ₈ O ₁₈	C ₁₀₄ H ₁₃₆ CoLi ₁₀ N ₄ O ₂₆	C ₁₆ H ₃₀ CoO ₉
Formula Weight	752.61	706.53	734.58	2009.82	1986.49	425.33
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>C</i> 2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P1	C2/c
$T (K)$ $a (Å)$ $b (Å)$ $c (Å)$ $\alpha (°)$ $\beta (°)$ $\gamma (°)$ $V (Å^{3})$	100	100	100	100	100	100
	26.2601(7)	6.8406(1)	13.7134(4)	23.0067(3)	15.577(2)	18.675(7)
	9.5962(3)	18.9481(3)	19.3125(6)	18.6293(3)	15.672(2)	7.944(2)
	16.4646(5)	12.6451(2)	14.6648(4)	24.8919(3)	23.368(2)	27.60(1)
	90	90	90	90	92.707(2)	90
	120.418(1)	95.478(1)	114.435(1)	110.293(1)	99.530(2)	109.59(2)
	90	90	90	90	99.094(2)	90
	3577.9(2)	1631.53(4)	3536.0(2)	10006.4(2)	5539.5(9)	3858(2)
$\begin{aligned} & \mathcal{L} \\ \rho_{\text{calc}} (\text{mg mm}^{-3}) \\ \mu (\text{mm}^{-1}) \\ F(0 \ 0 \ 0) \\ \lambda (\text{Å}) \\ & R_{\text{int}} \\ & R_1 \ (l > 2\sigma(l)) \\ & R_1 \ (\text{all data}) \\ & wR_2 \ (l > 2\sigma(l)) \\ & wR_2 \ (\text{all data}) \end{aligned}$	4	2	4	4	2	8
	1.397	1.438	1.380	1.334	1.191	1.465
	0.980	8.427	0.992	5.672	0.225	0.934
	1576	740	1544	4224	2106	1800
	0.71073	1.54178	0.71073	1.54178	0.71073	0.71073
	0.0146	0.0220	0.0399	0.0443	0.0749	0.0962
	0.0242	0.0267	0.0285	0.0337	0.0582	0.0346
	0.0261	0.0281	0.0377	0.0450	0.0988	0.0766
	0.0627	0.0681	0.0713	0.0794	0.1338	0.0597
	0.0636	0.0689	0.0763	0.0850	0.1504	0.0664

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

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$$^{b}wR_{2} = \sqrt{\sum \left[w\left(F_{o}^{2} - F_{c}^{2}\right)^{2}\right]} / \sum \left[w\left(F_{o}^{2}\right)^{2}\right]; w = \frac{1}{\left[\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP\right]}; P = \left[\max\left(0orF_{o}^{2}\right) + 2F_{c}^{2}\right] / 3.$$

and Rh₂(O₂CCPh₃)₄(κ^1 (Cl)-CH₂Cl₂)₂ [23], and axial ligand-free examples of each have been particularly difficult to characterize [24]. Though Cr₂(II,II) and Mo₂(II,II) systems have quadruple bonds between the metal atoms, they still react readily with oxygen to disrupt the paddlewheel structure. Of note, though, is that a similar issue is presumed to occur in catalyst arrest of Rh₂(O₂CR)₄ systems, which is ameliorated by use of the esp ligand [8,25].

Synthesis of Cr₂ and Mo₂ paddlewheel complexes was achieved 413 using carboxylate exchange reactions of the $M_2(OAc)_4$ species with 414 H₂esp. After the axial water ligands are removed from red Cr₂(-415 416 OAc)₄(H₂O)₂ under high vacuum at 100–110 °C, the brown anhy-417 drous Cr₂(OAc)₄ reacts with H₂esp in either THF or butyronitrile to quickly afford $Cr_2(esp)_2(L)_2$ complexes, **1**-2L. Brown blocks of 418 419 1.2THF grew in the triclinic space group *P*1 from solvent diffusion 420 of pentane into a concentrated toluene solution of the complex. 421 Orange plates of **1**-**2PrCN** grow in the monoclinic space group *P*2/ *n* from butyronitrile, and the asymmetric unit contains two uncon-422 nected half-molecules, where the Cr-Cr bonds are centered on 423 crystallographic inversion centers (Fig. 2). The crystal structure of 424

1.2THF contains a Cr-Cr distance of 2.2944(7) Å and 1.2PrCN pos-

sesses Cr-Cr distances of 2.3538(6) and 2.3178(6) Å, similar to

those in other known Cr₂ carboxylate complexes [6]. The Cr–O carboxylate distances are in the range 2.008(1)–2.024(1) Å for both complexes. The axial Cr–O distances of **1**·**2THF** are 2.3157(12) Å and the Cr–N distances of **1**·**2PrCN** are in line with those seen for other Cr₂(O₂CR)₄(MeCN)₂ compounds at 2.332(2) and 2.286(2) Å [24b].

In addition to equatorial ligand substitution from $Cr_2(OAc)_4$, the $Cr_2(esp)_2$ core is accessible via reaction of ethanolic H₂esp with aqueous Cr^{2+} . This synthetic method was explored based on a similar route used to access $Cr_2(OAc)_4(H_2O)_2$, in which Cr^{3+} (aq) is reduced to Cr^{2+} (aq) with zinc amalgam followed by exposure to aqueous sodium acetate [12b]. In our case, H₂esp was used rather than its sodium salt. While successful, this route is lower yielding than equatorial substitution from the acetate complex. Red blocks of the polymeric **1**·H₂esp structure grow via vapor diffusion of hexanes into a toluene solution of the compound (Scheme 2).

The crystals of $1 \cdot H_2 esp$ grow in the triclinic space group P1. The444structure consists of a chain of Cr_2 paddlewheel structures, cen-445tered on inversion centers, bridged by neutral $H_2 esp$ molecules446bound in the axial positions (Fig. 3). A carbonyl oxygen of the free447



Fig. 1. Coordination modes of the acetate ligand for Co complexes found within the Cambridge Structural Database.

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448 H₂esp carboxylic acid coordinates to the axial site of the $Cr_2(esp)_2$ 449 paddlewheel units, and the acidic proton is hydrogen bonded to a 450 proximal equatorial carboxylate oxygen atom $(0 \cdots 0$ distances are 451 2.67–2.70 Å). There are two crystallographically unique Cr_2 units, 452 each half present in the asymmetric unit, and one $Cr_2(esp)_2$ unit has positional disorder in the esp ligands. The Cr-O_{eq} and Cr-O_{ax} 453 454 distances of 1.958(5)-2.054(3) Å and 2.2736(9)-2.3064(8) Å, respectively, are in the expected range. The Cr-Cr distances for 455 the two Cr_2 units in the asymmetric unit are 2.2511(4) and 456 2.3515(4) Å. While both Cr-Cr distances are in the typical range 457 for quadruply-bonded Cr₂ carboxylate paddlewheel complexes 458 459 [6], it is remarkable that they differ by as much as 0.1 Å from each other. There are two effects at play here. First, weakening the Cr-Cr 460 461 σ bond via stronger σ -donation of the axial ligand has been 462 described in other Cr₂ tetracarboxylates [26], but we see the oppo-463 site effect here. The Cr₂(esp)₂ unit with the shorter Cr–Cr distances 464 has axial Cr–O_{ax} distances that are each 0.03 Å shorter than in the 465 $Cr_2(esp)_2$ unit with the longer metal-metal bond. However, the 466 HO-C=O_{ax}-Cr torsion angles involving the axial H₂esp ligands differ significantly, being larger by $\sim 10^{\circ}$ for the Cr₂(esp)₂ unit with 467 468 the shorter Cr–Cr bond. We suggest that the HO–C=O_{ax}–Cr torsion 469 angles affect the ability of the H₂esp ligand to act as a π donor to





the Cr_2 unit, binding in such a way as to disrupt the Cr- $Cr \pi$ bond.470Such π -donor interactions have been observed before with ligands471having specifically-oriented pyridine groups [27]. It appears that472this π effect is of greater magnitude in this case than the σ -dona-473tion effect.474

As with $Cr_2(esp)_2$, synthesis of $Mo_2(esp)_2$ (**2**) via carboxylate exchange from $Mo_2(OAc)_4$ was straightforward and high yielding. Following a method adapted from Cotton and coworkers [28], refluxing $Mo_2(OAc)_4$ in deoxygenated ethanol with H_2esp yielded a yellow solid consistent with its formulation as **2** by ¹H NMR spectroscopy (Scheme 3).

The ¹H NMR resonances are consistent with the D_{2h} symmetry expected for the compound, and shift slightly downfield from those of the parent acid, indicating removal of electron density from the ligand upon coordination to the metal, particularly the protons nearest the carboxylate group: the methyl resonances shift from 1.17 ppm for H₂esp to 1.44 ppm for **2** ($\Delta \delta$ = +0.27 ppm), and the methylene resonances from 2.84 ppm to 3.01 ppm ($\Delta \delta$ = +0.17 ppm). In comparison, the largest aryl resonance shift is only 0.06 ppm.

3.3. Co complexes of the esp ligand

The paddlewheel-type bimetallic tetracarboxylate structure is very well known for Rh₂ complexes, with >470 structurally characterized examples in the CSD [29]. In comparison, relatively few, only 32, Co₂ carboxylate paddlewheel structures are present in the CSD [11,30]. We recently reported the first example of a Co₂ paddlewheel-type complex supported with the esp ligand [10]. This complex, Co₂(esp)₂(EtOH)₂ (**3**·**2EtOH**), is obtained in useful yields and is therefore of great utility in the preparation of further examples of esp-supported Co₂ compounds. In particular, we were curious to see whether it would be possible to perform axial ligand substitution reactions on the Co₂(esp)₂ unit. One of the keys to the success of Rh₂-tetracarboxylates as catalysts is their ability to undergo facile axial ligand substitution while retaining the paddlewheel structure of the equatorial ligands. Thus, a prerequisite for any potential development of Co₂ catalysts is to see whether axial ligand substitution can be achieved with retention of the equatorial ligands and the paddlewheel geometry.

In this work, we have found that axial ligand substitution of 3-2EtOH can occur, with some limitations. We found that the axial ethanol molecules could be easily substituted for either acetonitrile or water, depending on how the ethanol adduct is processed after synthesis. The acetonitrile adduct **3 2CH₃CN** may be obtained by soaking crystals of the ethanol adduct in acetonitrile in air, and, though the complex does not noticeably dissolve, the crystals change in color from black to blue in what appears to be a single crystal-to-single crystal transformation. The blue crystals have the monoclinic space group C2/c, with the Co···Co vector centered on a crystallographic inversion center (Fig. 4A). The Co--Co distance is 2.6962(4) A, shorter than with axial ethanol molecules but also too long to be considered a full Co-Co bond. For comparison, the few known structures with genuine Co-Co single bonds have separations of 2.26–2.38 Å [31]. Like in Co₂(esp)₂(EtOH)₂, the two Co-Lax vectors are parallel but not coaxial: the Co-Co-N angle is 177°.

When 3-2EtOH is dissolved in methylene chloride and is layered 525 with diethyl ether, purple plates of **3**·2**H**₂**O** grow over two days. 526 These crystals form in the monoclinic space group $P2_1/c$ and the 527 paddlewheel units lie on crystallographic inversion centers within 528 the structure (Fig. 4B). The Co–Co distance is 2.6868(3) Å – the 529 shortest separation amongst the $Co_2(esp)_2L_2$ complexes – and the 530 Co-Co-O_{ax} angle is 173°. The geometric parameters for the three 531 $Co_2(esp)_2L_2$ complexes are summarized and compared in Table 3. 532 The Co–O distances to the esp ligands are all ~2.04 Å for both com-533

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Scheme 2.



Fig. 3. Thermal ellipsoid plot of $1 \cdot H_2 esp$ with ellipsoids drawn at the 50% probability level. One of two crystallographically independent Cr₂ paddlewheel units is shown in full; dashed atoms represent where the polymer structure continues. A solvate toluene molecule is not shown; non-CO₂H hydrogen atoms have been omitted for clarity.

 $Mo_2(OAc)_4 \xrightarrow{2 H_2 esp, EtOH} Mo_2(esp)_2 + 4 HOAc$ Scheme 3.

pounds, similar to those in **3·2EtOH**. Magnetic studies of the latter
complex indicate that both Co(II) ions are high-spin [10], and we
may safely assume that the acetonitrile and water adducts behave
likewise.

It is noteworthy that these Co₂ complexes possess relatively 538 539 small molecules as axial ligands: ethanol, acetonitrile, and water. The previous examples of molecular Co₂(esp)₂(L)₂ structures con-540 541 sistently possess bulky N-donor heterocyclic axial ligands such as quinoline [11], which have been believed to be necessary to pre-542 vent formation of oligomeric Con species. Thus, the esp ligand 543 allows us to stabilize the discrete, bimetallic Co₂(O₂CR)₄ unit to 544 545 axial ligand exchange reactions using smaller axial ligands than previously possible and, notably, O-donor ligands in addition to 546 N-donors. 547

Unfortunately, stabilization of the Co₂ paddlewheel structure by 548 549 esp is not failsafe. In studying 3 2EtOH, we found that the struc-550 tural stability can be compromised by certain solvents, growth rates of crystals, and minor impurities. Two examples of solvents 551 552 that disrupt the paddlewheel structure are methanol and pyridine. Slow evaporation of a methanol solution of **3**·**2EtOH** yields purple 553 crystals of a one-dimensional Co/esp/MeOH structure with formula 554 555 $Co_2(esp)_2(MeOH)_2$, **4**, in the monoclinic space group $P2_1/c$ (Fig. 5A). 556 Though the stoichiometry for this structure is similar to the 557 adducts of 3 with ethanol, acetonitrile, or water, the structure of 558 4 is different. The two arms of the esp ligand adopt different coor-559 dination modes: while one arm is bridging as usual, the other arm 560 adopts coordination mode D from Fig. 1. The two Co(II) ions there-561 fore adopt different coordination geometries, one six-coordinate and the other five coordinate (trigonal bipyramidal). Pyridine, 562



Fig. 4. Crystal structures of **3·2CH₃CN** (A) and **3·2H₂O** (B) with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms except on the water molecules have been omitted for clarity.

too, disrupts the paddlewheel structure, which was somewhat surprising to us considering the prevalence of reported quinoline-stabilized structures of monocarboxylates. When 3-2EtOH is dissolved in pyridine in air, evaporation of the resulting solution yields very large red block-shaped crystals. The crystals contain a binuclear $Co_2(py)_4(esp)_2(H_2O)$ cluster, **5**, in the monoclinic space group $P2_1/c$ (Fig. 5 B). Previous reports, though lacking some experimental details, seem to indicate that guinoline and other bulky heterocyclic compounds were used only in stoichiometric amounts, whereas pyridine was used in large excess in this case, leading to degradation of the paddlewheel-type structure. Another factor likely leading to the collapse of the paddlewheel-type structure is the inclusion of a water molecule bridging between the two Co (II) ions. This water molecule is engaged in two hydrogen bonds $(0 \cdots 0 \text{ distances of } 2.53-2.59 \text{ Å})$ to the esp ligands causing each ligand to have a monodentate (Fig. 1 B) coordination mode for one arm.

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Table 3			
Summary of	Co ₂ (esp) ₂ L ₂	bond	lengths.

Complex	Co-Co distance (Å)	Co–O _{eq} avg. distance (Å)	Co–L _{ax} distance(s) (Å)	Co–Co–L _{ax} angle (°)	Reference
3·2H ₂ O	2.6868(3)	2.04(4)	2.004(1)	173.07(4)	This work
3·2CH ₃ CN	2.6962(4)	2.03(1)	2.070(1)	176.57(4)	This work
3·2EtOH	2.74(2)	2.04(3)	2.02(2)	164(3)	[10]



to absorb enough water from the air to form this complex. In the structure of **6**, one of the esp carboxylate arms "slips" from the original μ_2 -OCO' mode into a $\kappa^1 O/\mu_2$ -O' mode (Fig. 1D), though this change is likely the result of the desire of Co²⁺ to be five coordinate in the absence of a suitable exogenous capping axial ligand. Other paddlewheel-type carboxylate compounds fulfill the need for axial ligands by self-association binding a carboxylate O atom from a neighboring M₂(O₂CR)₄ molecule [33], but this type of structural aggregation is not observed for Co₂ carboxylates. Furthermore, square planar and square pyramidal Co²⁺ complexes supported only by O-donor ligands are known but rare [34], emphasizing the preference for a five-coordinate structure.

We also report here initial experiments in which Co(II) starting materials were combined with the H₂esp ligand to yield non-paddlewheel-type structures. The use of an alkali metal salt of the esp



Fig. 5. X-ray structures that arise from the growth of crystals from a solution of **3-2EtOH** in MeOH (A) and pyridine (B). Thermal ellipsoids are represented at the 50% probability level. For **4** (A), two of the repeating unit are shown, and all hydrogen atoms are omitted for clarity, except the methanol alcoholic protons. For **5** (B), for clarity, only one of the two [Co₂] units in the asymmetric unit is shown and all hydrogen atoms are omitted except those on the aquo ligand (O9).

The speed with which a solution of Co₂(esp)₂ is concentrated 580 was also found to affect the molecular structures found in the crys-581 tals of Co₂ complexes. While slow crystal growth from layering a 582 CH₂Cl₂ solution of **3**·2EtOH with diethyl ether led to the **3**·2H₂O 583 structure, rapid growth, induced by mixing the two solvents, 584 585 resulted in a one-dimensional polymeric structure with the molecular formula of $[Co(esp)]_n$, **6** [32]. One can hypothesize that the 586 quicker growth under these conditions precluded growth of the 587 588 bis-water adduct as time is needed for the CH₂Cl₂/Et₂O mixture



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Fig. 6. Thermal ellipsoid plots of the repeat unit of the one-dimensional polymer **7**, with ellipsoids drawn at the 50% probability level. Interstitial acetonitrile molecules and all hydrogen atoms except those on the water moieties have been omitted for clarity. (A) Side view, with esp ligands truncated except for the carboxylate groups and α carbons, the latter of which are shown as dashed ellipsoids; (B) End-on view of the polymer, with full esp ligands shown and their carbon atoms and bonds shown in grey.

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Scheme 4.



Fig. 7. X-ray crystal structure showing several repeat units of **8**, with thermal ellipsoids drawn at the 50% probability level. The asymmetric unit contains one esp ligand, two half-occupied Co centers, three bound water molecules, and two interstitial water molecules that are hydrogen bonded to the lattice. Non-water hydrogen atoms and the interstitial water molecules (O8 and O9) are omitted for clarity.



Fig. 8. IR signal of (4-methoxyphenyl)diazoacetate methyl ester in solution over time in the presence of no additive, $10 \text{ mol}\% \text{ Cr}_2(\text{esp})_2(\text{THF})_2$, or $10 \text{ mol}\% \text{ Co}_2(\text{esp})_2(\text{EtOH})_2$.

ligand was explored, starting with deprotonation of the H₂esp free acid by ⁿBuLi followed by addition of anhydrous CoCl₂ in THF. After work-up, purple plate-shaped crystals of a one-dimensional polymer of the formula $[CoLi_{10}(esp)_6(H_2O)_2(CH_3CN)]_n$, **7**, in the *P*¹ space group grew by slow evaporation of an acetonitrile solution. The polymer repeat unit in **7** contains one tetrahedral Co²⁺ cen-

ter, ten tetrahedral Li⁺ ions, and six esp²⁻ ligands holding a chain of the cations together, and two coordinated water molecules, along with one coordinated and three interstitial acetonitrile molecules (Fig. 6). The Co(II) center is coordinated in a rough tetrahedron of oxygen atoms, coordinating with one oxygen atom per carboxylate



Fig. 9. Proposed catalytic cycle of diazo cyclopropanation with Co₂(esp)₂.

group of four esp ligands. There are also two nearby lithium ions, 2.74 and 2.75 Å away, connected through bridging carboxylate oxygen atoms.

Since the solubility of LiCl led to the formation of **7**, CoSO₄ was combined with the barium salt of esp (Scheme 4), relying on the insolubility of BaSO₄ to ensure that the only ions in solution were Co^{2+} and esp^{2-} . However, the structure of the resulting compound, $Co(esp)(H_2O)_3$, **8**, does not contain the desired paddlewheel unit. After the BaSO₄ precipitate was removed, the material was dried under vacuum and reconstituted in CH_2Cl_2 , from which pink plate-shaped crystals formed that contain a two-dimensional web of cobalt ions, esp ligands, and water molecules (Fig. 7). The structure contains chains of alternating cobalt centers – on crystallographic inversion centers – and esp ligands, and the chains are held together by bridging water molecules that link the cobalt centers from one chain to the next. Again, it appears that the paddlewheel structure is in competition with other kinetic or thermodynamic products.

In total, these structural studies serve to highlight the challenges of Co coordination chemistry as they relate to the proposition of forming complexes stable enough to serve as catalysts analogous to the Rh₂ carboxylates. The Co carboxylates can, under the right conditions, mimic the ligand substitution chemistry of Rh₂ complexes, with the axial ligands being more labile than the equatorial carboxylate ligands. However, the Co carboxylate groups are also labile and can adopt a number of coordination geometries that are not observed in the analogous Rh₂ compounds. We may attribute this effect partly to the high-spin nature of the Co(II) ions in the Co₂(esp)₂ structures.

3.4. Preliminary catalytic reactivity of $Co_2(esp)_2$ and $Cr_2(esp)_2$ complexes with diazo compounds

The new paddlewheel-type complexes reported here were tested for their ability to decompose organic diazo compounds. The reaction of either $Co_2(esp)_2(EtOH)_2$ or $Cr_2(esp)_2(THF)_2$ with (4-methoxyphenyl)diazoacetate methyl ester produced no visible effervescence that would suggest formation of N_2 , so we investi-

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651 gated the reaction using *in situ* IR spectroscopy. We monitored the 652 diazo stretch at 2085 cm⁻¹ over time in the presence of the carbene 653 trap styrene (Fig. 8). As compared with a control reaction where no 654 metal complex was present, $Co_2(esp)_2(EtOH)_2$ shows a burst of 655 reactivity within the first 2.25 h, and $Cr_2(esp)_2(THF)_2$ seemed to behave identically to the control experiment. For the Co₂ catalyst, 656 657 the diazo concentration goes down by 40% within the first 2.25 h, indicative of catalytic activity of the compound, but the subse-658 quent loss of activity indicates catalyst arrest. 659

In order to determine the effectiveness of the complexes for catalytic cyclopropanation, the reaction of (4-bromophenyl)diazoacetate methyl ester with styrene was performed in the presence of Mo₂(esp)₂, Cr₂(esp)₂(THF)₂, or Co₂(esp)₂(EtOH)₂ at catalyst loadings of 10 mol% and the crude reaction mixtures were subjected to 665 analysis by ¹H NMR spectroscopy. The reactions mixtures that utilized either $Mo_2(esp)_2$ or $Cr_2(esp)_2(THF)_2$ did not differ from the control where no metal complex was present. However, the reaction involving the complex $Co_2(esp)_2(EtOH)_2$ provided the desired cyclopropanation product in 71% spectroscopic yield and this product was isolated by column chromatography in 49% yield.

671 In analogy to cyclopropanation reactions catalyzed by Rh car-672 boxylate dimers, we may propose a carbenoid, $Co \cdot \cdot \cdot Co = CR_2$, inter-673 mediate as the reactive intermediate in catalysis (Fig. 9). The 674 potential generation of a Co-Co bond upon formation of the puta-675 tive carbene complex intermediate, and the implications of this 676 issue in the catalytic process are currently under investigation.

4. Summary.

678 In this work, we report the preparation and characterization of Cr₂, Mo₂, and Co₂ paddlewheel-type complexes supported by the 679 chelating dicarboxylate ligand esp. The Co₂ complex is not as struc-680 681 turally rigid as the Cr2 or Mo2 complexes, and Co(II) complexes displaying a variety of alternative coordination modes have been 682 683 prepared. Nevertheless, the $Co_2(esp)_2(EtOH)_2$ complex does show 684 some activity for the decomposition of the organic diazo com-685 pound methyl 4-bromophenyldiazoacetate, suggesting that further 686 modifications to the Co₂ structure may lead to new catalysts for 687 carbenoid chemistry.

Acknowledgments 688

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696 Appendix A. Supplementary data

697 Supplementary data to this article can be found online at 698 https://doi.org/10.1016/j.poly.2018.12.045.

References 699

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- 700 [1] (a) H.M.L. Davies, J.R. Manning, Nature 451 (2008) 417; 701
 - (b) M.P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, Chem. Rev. 110 (2010) 704;
 - (c) H.M.L. Davies, D. Morton, Chem. Soc. Rev. 40 (2011) 1857;
 - (d) H.M.L. Davies, R.E.J. Beckwith, Chem. Rev. 103 (2003) 2861;
 - (e) J. Du Bois, Org. Proc. Res. Dev. 15 (2011) 758;
 - (f) K.P. Kornecki, J.F. Berry, D.C. Powers, T. Ritter, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, 2014, p. 225.
 - [2] (a) A.R. Corcos, J.S. Pap, T. Yang, J.F. Berry, J. Am. Chem. Soc. 138 (2016) 10032; (b) S. Goberna-Ferron, B. Pena, J. Soriano-Lopez, J.J. Carbo, H. Zhao, J.M. Poblet, K.R. Dunbar, J. Ramon Galan-Mascaros, J. Catalysis 315 (2014) 25;
 - (c) L. Villalobos, J.E.B. Paredes, Z. Cao, T. Ren, Inorg. Chem. 52 (2013) 12545.

- [3] M.E. Harvey, D.G. Musaev, J. Du Bois, J. Am. Chem. Soc. 133 (2011) 17207.
- [4] D.C. Powers, T. Ritter, Nat. Chem. 1 (2009) 302.
- [5] (a) I.G. Powers, C. Uyeda, ACS Catal. 7 (2017) 936;
- (b) B.G. Cooper, J.W. Napoline, C.M. Thomas, Catal. Rev. Sci. Eng. 54 (2012) 1. [6] F.A. Cotton, C.A. Murillo, R.A. Walton, Multiple Bonds Between Metal Atoms, 3rd ed., Springer Science and Business Media Inc, New York, 2005.
- [7] (a) J. Hansen, B. Li, E. Dikarev, J. Autschbach, H.M.L. Davies, Journal of Organic Chemistry 74 (2009) 6564;
 - (b) T.L. Sunderland, J.F. Berry, Dalton Trans. 45 (2016) 50; (c) T.L. Sunderland, J.F. Berry, Journal of Coordination Chemistry 69 (2016) 1949.

(d) T.L. Sunderland, J.F. Berry, Chemistry-a European Journal 22 (2016) 18564; (e) Z. Ren, T.L. Sunderland, C. Tortoreto, J.F. Berry, D.G. Musaev, H.M.L. Davies, Submitted.

- [8] C.G. Espino, K.W. Fiori, M. Kim, J. Du Bois, J. Am. Chem. Soc. 126 (2004) 15378.
- (a) M.Q. Dequeant, P.E. Fanwick, T. Ren, Inorg. Chim. Acta 359 (2006) 4191; (b) Y.L. Tnay, C. Chen, Y.Y. Chua, L.N. Zhang, S. Chiba, Org. Lett. 14 (2012) 3550.
- [10] R.J. Pakula, J.F. Berry, Dalton Trans. 47 (2018) 13887.
- [11] (a) J.E. Davies, A.V. Rivera, G.M. Sheldrick, Acta Crystallogr. B 33 (1977) 156; (b) J. Hudak, R. Boca, L. Dlhan, J. Kozisek, J. Moncol, Polyhedron 30 (2011) 1367: (c) J. Catterick, M.B. Hursthouse, P. Thornton, A.J. Welch, J. Chem. Soc. Dalton Trans. (1977) 223:
 - (d) H. Abu Ali, A. Abu Shamma, S. Kamel, J. Mol. Str. 1142 (2017) 40; (e) Y. Cui, F.K. Zheng, J.S. Huang, Acta Crystallogr. C 55 (1999) 1067;
 - (f) Y. Cui, D.L. Long, X.Y. Huang, F.K. Zheng, W.D. Chen, J.S. Huang, Chin. J. Struct. Chem. 18 (1999) 9.
- [12] (a), Inorganic Syntheses Vol. 3 (1950) 148; (b) R.E. Da Re, J.L. Eglin, C.N. Carlson, K.D. John, D.E. Morris, W.H. Woodruff, J.A. Bailey, E. Batista, R.L. Martin, F.A. Cotton, E.A. Hillard, C.A. Murillo, A.P. Sattelberger, R.J. Donohoe, J. Am. Chem. Soc. 132 (2010) 1839.
- [13] C.M. Qin, V. Boyarskikh, J.H. Hansen, K.I. Hardcastle, D.G. Musaev, H.M.L. Davies, J. Am. Chem. Soc. 133 (2011) 19198.
- [14] Bruker SMART Program, Bruker AXS, Inc., Madison, WI, USA, 2013. [15] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl.
- Crystallogr. 42 (2009) 339. [16] (a) G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112;
 - (b) G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3.
- [17] A.L. Spek, Acta Crystallogr. C 71 (2015) 9.
- [18] (a) A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7;
- (b) A.L. Spek, Acta Crystallographica. D 65 (2009) 148.
- [19] J.E. Barker, T. Ren, Inorg. Chem. 47 (2008) 2264.
- [20] R.J. Pakula, M. Srebro-Hooper, C.G. Fry, H.J. Reich, J. Autschbach, J.F. Berry, Inorg. Chem. in press. [21] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic
- Chemistry, 6th ed., Wiley, New York, 1999. [22] J.F. Berry, Dalton Trans. 41 (2012) 700.
- [23] (a) F.A. Cotton, X.J. Feng, P.A. Kibala, M. Matusz, J. Am. Chem. Soc. 110 (1988) 2807:
- (b) K.P. Kornecki, J.F. Briones, V. Boyarskikh, F. Fullilove, J. Autschbach, K.E. Schrote, K.M. Lancaster, H.M.L. Davies, J.F. Berry, Science 342 (2013) 351.
- [24] (a) F.A. Cotton, E.A. Hillard, C.A. Murillo, J. Am. Chem. Soc. 124 (2002) 5658;
 (b) F.A. Cotton, E.A. Hillard, C.A. Murillo, H.C. Zhou, J. Am. Chem. Soc. 122 (2000) 416.
- [25] (a) K.W. Fiori, J. Du Bois, J. Am. Chem. Soc. 129 (2007) 562;
- (b) D.N. Zalatan, J. Du Bois, J. Am. Chem. Soc. 131 (2009) 7558.
- [26] F.A. Cotton, W. Wang, Nouveau Journal De Chimie-New J. Chem. 8 (1984) 331. [27] F.A. Cotton, L.M. Daniels, C.A. Murillo, I. Pascual, H.C. Zhou, J. Am. Chem. Soc.
- 121 (1999) 6856 [28] F.A. Cotton, T.S. Barnard, L.M. Daniels, C.A. Murillo, Inorg. Chem. Commun. 5
- (2002) 527. [29] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, Acta Crystallogr. B 72 (2016)
- 171. [30] (a) G.F.S. Whitehead, J. Ferrando-Soria, L. Carthy, R.G. Pritchard, S.J. Teat, G.A. Timco, R.E.P. Winpenny, Dalton Trans. 45 (2016) 1638; (b) T. Hokelek, E.G. Saglam, B. Tercan, O. Aybirdi, H. Necefoglu, Acta Crystallogr. E 67 (2011) M28; (c) D.H. Wang, X. Li, X.G. Liu, Acta Crystallogr. E 60 (2004) M703; (d) T.S. Gifeisman, A.A. Dvorkin, G.A. Timko, U.A. Simonov, N.V. Gerbeleu, G.A. Popovich, Izv. Akad. Nauk Mold. SSR Ser. Fiz. Tekh. Mat. Nauk 22 (1985) 2; (e) P.A. Ajibade, G.A. Kolawole, P. O'Brien, J. Raftery, M. Helliwell, J. Coord. Chem. 61 (2008) 328: (f) N. Benbellat, K.S. Gavrilenko, Y. Le Gal, O. Cador, S. Golhen, A. Gouasmia, J. M. Fabre, L. Ouahab, Inorg. Chem. 45 (2006) 10440;
 - (g) S.A. Hilderbrand, S.J. Lippard, Inorg. Chem. 43 (2004) 5294; (h) X.J. Lei, M.Y. Shang, T.P. Fehlner, R. Werner, W. Haase, D. Hautot, G.J. Long,
 - J. Organomet. Chem. 541 (1997) 57;

(i) S.E. Nefedov, T.O. Denisova, Z.B. Dobrokhotova, F.M. Dolgushin, G.V. Romanenko, V.N. Ikorskii, V.I. Ovcharenko, Russ. J. Inorg. Chem. 51 (2006) 1587:

- (j) M. Benslimane, Y.K. Redjel, G. Denes, H. Merazig, Acta Crystallogr. E 69 (2013) m517;
- (k) A.A. Pasynskii, S.S. Shapovalov, A.V. Gordienko, I.V. Skabitskii, Russ. J. Coord. Chem. 37 (2011) 127;
- (1) E.V. Pakhmutova, A.E. Malkov, T.B. Mikhailova, A.A. Sidorov, I.G. Fomina, G. G. Aleksandrov, V.M. Novotortsev, V.N. Ikorskii, I.L. Eremenko, Russ. Chem.

- (m) T.O. Denisova, Z.B. Dobrokhotova, V.N. Ikorskii, S.E. Nefedov, Russ. J. Inorg.
 (m) T.O. Denisova, Z.B. Obbrokhotova, V.N. Ikorskii, S.E. Nefedov, Russ. J. Inorg.
 (chem. 51 (2006) 1363;
- 800 (n) S.E. Nefedov, E.S. Chernetsova, A.A. Sidorov, S.L. loffe, Dokl. Chem. 377 801 (2001) 108;
- 802 (o) Y.S. Wang, Z.M. Zhou, J. Solid State Chem. 228 (2015) 117;
- 803 (p) J. Qin, F.X. Li, L. Xue, N. Lei, Q.L. Ren, D.Y. Wang, H.L. Zhu, Acta Chim. Slov.
 804 61 (2014) 170;
- 805 (q) P.K. Chen, Y. Qi, Y.X. Che, J.M. Zheng, Cryst. Eng. Comm. 12 (2010) 720;
- (r) N. Klein, I. Senkovska, I.A. Baburin, R. Grunker, U. Stoeck, M.
 Schlichtenmayer, B. Streppel, U. Mueller, S. Leoni, M. Hirscher, S. Kaskel,
 Chem. Eur. J. 17 (2011) 13007;
- 809 (s) Q.X. Yao, J.L. Sun, K. Li, J. Su, M.V. Peskov, X.D. Zou, Dalton Trans. 41 (2012)
 810 3953;
- (t) L.P. Hsu, J.Y. Wu, K.L. Lu, J. Inorg. Organomet. Polym. Mater. 17 (2007) 259;
 (u) S.W. Lee, H.J. Kim, Y.K. Lee, K. Park, J.H. Son, Y.U. Kwon, Inorg. Chim. Acta 253 (2003) 151.
- 813 353 (2003) 151;
 814 (v) Q. Zhou, S. Zhang, H. Song, L. Yue, Y. Wang, J. Synth. Cryst. (2004) 395;
- (v) Q. Zhou, S. Zhang, H. Song, L. Fue, F. Wang, J. Synth. Cryst. (2004) 395,
 (w) I.H. Park, H. Ju, T.S. Herng, Y. Kang, S.S. Lee, J. Ding, J.J. Vittal, Cryst. Growth
 Design 16 (2016) 7278;
- 817 (x) H. Chun, H.J. Jung, J.W. Seo, Inorg. Chem. 48 (2009) 2043;
- (y) E.Y. Choi, K. Park, C.M. Yang, H. Kim, J.H. Son, S.W. Lee, Y.H. Lee, D. Min, Y.U. 819 Kwon, Chem. Eur. J. 10 (2004) 5535;
- 820 (z) Y. Qi, Y. Wang, Inorg. Chem. Commun. 35 (2013) 83;
- 821 (a) R.Y. Zou, P.Z. Li, Y.F. Zeng, J. Liu, R. Zhao, H. Duan, Z. Luo, J.G. Wang, R.Q.
- 822 Zou, Y.L. Zhao, Small 12 (2016) 2334;
- (ab) Z.J. Zhang, L.P. Zhang, L. Wojtas, M. Eddaoudi, M.J. Zaworotko, J. Am.
 Chem. Soc. 134 (2012) 928.

 [31] (a) F.A. Cotton, L.M. Daniels, X.J. Feng, D.J. Maloney, J.H. Matonic, C.A. Murillo, Inorg. Chim. Acta 256 (1997) 291;
 (b) L.P. He, C.L. Yao, M. Naris, J.C. Lee, J.D. Korp, J.L. Bear, Inorg. Chem. 31

(1992) 620; (c) F.A. Cotton, Z. Li, C.A. Murillo, P.V. Poplaukhin, J.H. Reibenspies, J. Cluster Sci. 19 (2008) 89;

- (d) F.A. Cotton, R. Poli, Inorg. Chem. 26 (1987) 3652;
- (e) G.M. Lin, M. Sigrist, E.C. Horng, C.H. Chen, C.Y. Yeh, G.H. Lee, S.M. Peng, Z. Anorg, Allg. Chem. 641 (2015) 2258;

(f) A. Klanicova, Z. Travnicek, I. Popa, M. Cajan, K. Dolezal, Polyhedron 25 (2006) 1421.

- [32] The crystallographic data for this structure were poor, but allowed us to determine the molecular connectivity. Formula: C32H40Co208, Orthorhombic, Pna21, Z = 4, a = 23.114(1) Å, b = 20.185(1) Å, c = 7.0134(4) Å, V = 3272.0(3) Å3.
- [33] (a) D.V. Baxter, R.H. Cayton, M.H. Chisholm, J.C. Huffman, E.F. Putilina, S.L. Tagg, J.L. Wesemann, J.W. Zwanziger, F.D. Darrington, J. Am. Chem. Soc. 116 (1994) 4551;
- (b) F.A. Cotton, E.V. Dikarev, X.J. Feng, Inorg. Chim. Acta 237 (1995) 19.
 [34] (a) L. Tahsini, S.E. Specht, J.S. Lum, J.J.M. Nelson, A.F. Long, J.A. Golen, A.L.

Rheingold, L.H. Doerrer, Inorg. Chem. 52 (2013) 14050;
(b) S.J. Obrey, S.G. Bott, A.R. Barron, Inorg. Chem. 41 (2002) 571;
(c) M.C. Hong, F.L. Jiang, X.Y. Huang, W.P. Su, W.J. Li, R. Cao, H.Q. Liu, Inorg. Chim. Acta 256 (1997) 137;
(d) G.H. Spikes, C. Milsmann, E. Bill, T. Weyhermuller, K. Wieghardt, Inorg. Chem. 47 (2008) 11745;

(e) V.D. Vreshch, J.H. Yang, H.T. Zhang, A.S. Filatov, E.V. Dikarev, Inorg. Chem. 49 (2010) 8430.

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