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An Efficient Synthesis of Acetylide/Trimetal/Acetylide Molecular Wires

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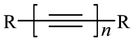
Efficient syntheses are reported for incorporating trimetal units of the type $M_3(dpa)_4^{2+}$ (M = Cr, Co, Ni, and dpa = 2,2′-dipyridylamide) into polyalkynyl assemblies to give the prototypical bis-phenylacetylide complexes $M_3(dpa)_4(CCPh)_2$. Reactions of $M_3(dpa)_4Cl_2$ with LiCCPh have led only to mixtures of products which cocrystallize forming materials of the composition $M_3(dpa)_4(CCPh)_xCl_{2-x}$. Here we report that acetonitrile complexes $[M_3(dpa)_4(NCCH_3)_2](PF_6)_2$ react cleanly with LiCCPh in MeCN to afford the desired target molecules in 40–60% yield and in excellent purity. Isolation of the mixed ligand complex $[Co_3(dpa)_4(NCCH_3)(CCPh)]PF_6$ has been accomplished, which suggests that these reactions are stepwise and that it will be possible to synthesize mixed acetylide complexes (i.e., $M_3(dpa)_4(CCR)(CCR')$) via this method.

Introduction

Molecular wires are a *sine qua non* of molecule-scale electronics.[1] Without the existence of molecule-scale entities having the ability to shuttle electrons across nanometer distances, molecular circuits and devices will be impossible to make. Among the candidates under consideration as useful molecular conductors, each with its own advantages or disadvantages,[1a] one of the most promising types involves conducting polyunsaturated moieties such as poly-ynes shown as **I**.[2]

Metal-capped species such as **II** have been synthesized,[3] and the alkynyl bridges have been shown to facilitate electron transfer from one terminal metal atom to the other.[4] These are known with various transition metal end caps,[5] as well as metal−metal bonded Ru_2^{5+} units.[6]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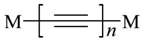
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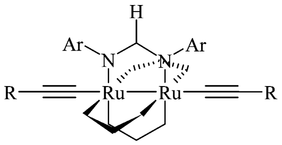
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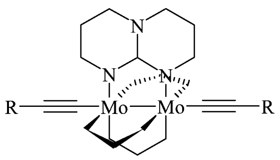
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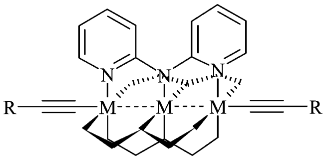
V

The study of molecular wires in this laboratory has focused on the smallest possible analogue of a macroscopic wire: a linear chain of single metal atoms each in direct contact with its neighbors.[7] The ligand dpa (the anion of 2,2′-dipyridylamine) stabilizes chains of three divalent metal atoms in complexes of the type $M_3(dpa)_4Cl_2$ (with M = Cr,[8] Co,[9] Ni,[10]

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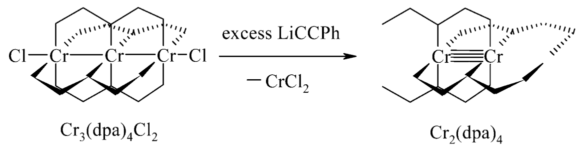
Cu,[11] Ru,[12] and Rh[12]). The electronic structures of these complexes and their one-electron oxidized analogues are fairly well understood[13] and show that for some, e.g., symmetrical Cr_3^{6+} and Co_3^{6+} complexes, delocalization across the trimetal chain is expected whereas Cu_3^{6+} species having no metal−metal bonds would be insulators. Complexes incorporating the $Cr_3^{6+/7+}$ or $Ni_3^{6+/7+}$ couples are possible molecular switches since delocalized states (symmetrical Cr_3^{6+} and Ni_3^{7+}) are available from the localized states via an applied potential. Actual employment of these (or any other) molecular wires will require the evaluation of ways to attach the ends of the wires to other elements in a molecular circuit. The use of alkynyl axial ligands is one of the most promising ways currently under consideration to do this. Since there is considerable acetylide chemistry known for Ru−Ru bonded units[14] (such as **III** having diarylformamidinate bridging ligands) and acetylide complexes of the Mo_2^{6+} or W_2^{6+} core (**IV** having 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidineate as the bridging ligand) have been contemplated,[15] the trinuclear molecules **V** with the bridging ligand 2,2′-dipyridylamide (dpa) are important prototypes because they are the simplest examples of a potentially large class of molecules containing extended metal atom chains (EMACs) which can be increased in length and modified in their properties by placing substituents on the wrapping ligands.[7]

We have undertaken systematic exploratory work to find out how to achieve controlled axial substitutions of Co_3^{6+}, Ni_3^{6+}, and Cr_3^{6+} complexes,[16] and here we report the synthesis of Cr_3, Co_3, and Ni_3 complexes with axial phenylacetylide ligands. $Cr_3(dpa)_4(CCPh)_2$ has been previously reported,[17] but the structure is not entirely correct as will be discussed in this paper. $Ni_3(dpa)_4(CCPh)_2$ has also been previously reported,[16b] but here an alternative and reliable synthetic method is given as well as an independent crystal structure with different interstitial solvent molecules.

Scheme 1



Results and Discussion

Synthesis. Efforts to prepare $Cr_3(dpa)_4(CCPh)_2$ by reaction of $Cr_3(dpa)_4Cl_2$ with excess lithium phenylacetylide in THF lead to a mixture of the target compound and the starting material in low yield.[17] In efforts to reproduce and optimize this reaction, we have found that the major product is the red dinuclear complex $Cr_2(dpa)_4$,[18] resulting from loss of one of the three chromium atoms, as shown in Scheme 1.

To gain further insight into the reactivity of the trimetal complexes toward acetylide ligands in a system which is more stable in air and easier to handle, we recently examined the analogous trinickel system.[16b] Again, reactions of $Ni_3(dpa)_4Cl_2$ with phenyl acetylide ions generated only mixed ligand complexes as shown in eq 1.

$$Ni_3(dpa)_4Cl_2 + HCCPh + \text{base} \rightarrow Ni_3(dpa)_4(CCPh)_xCl_{2-x} \quad (1)$$

The mixed ligand substances such as $Ni_3(dpa)_4(CCPh)_xCl_{2-x}$ were characterized crystallographically by the observation of unusual thermal parameters for the acetylide carbon atoms. Since $Cr_3(dpa)_4(CCPh)_2$ was originally prepared in a manner akin to that in eq 1,[17] we thought that the structure might also have some partially occupied axial chloride ions which may have been overlooked before. Reinvestigation of this structure using the previously collected data has shown this to be true (vide infra), and the correct formulation of this substance is $Cr_3(dpa)_4(CCPh)_{1.8}Cl_{0.2}$.

Thus, chloride ions must be meticulously removed from the reaction in order to produce pure samples of $M_3(dpa)_4(CCPh)_2$. For example, the acetonitrile complex $[Ni_3(dpa)_4(NCCH_3)_2](PF_6)_2$ was found to be the key starting material which made this chemistry possible as shown in eq 2.

$$[Ni_3(dpa)_4(NCCH_3)_2](PF_6)_2 + \text{excess } HCCPh + 2NaOH \rightarrow Ni_3(dpa)_4(CCPh)_2 \quad (2)$$

Unfortunately, this process is not general since the analogous Co_3^{6+} and Cr_3^{6+} starting complexes are not stable under the reaction conditions. In our search for an alternative route, the $[M_3(dpa)_4(NCCH_3)_2](PF_6)_2$ species were allowed to react with lithium phenylacetylide in THF solution. While the presence of $M_3(dpa)_4(CCPh)_2$ products was shown

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(18) $Cr_2(dpa)_4$ has been reported previously, and was identified crystallographically in this work. See: (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Pascual, I.; Zhou, H.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6856. (b) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L.; Smeets, W. J. J.; Chiang, M. Y. *J. Chem. Soc., Dalton Trans.* **1993**, 789.

spectroscopically, these solutions quickly decomposed; poor yields and low purity resulted. However, reaction of $[Co_3(dpa)_4(NCCH_3)_2](PF_6)_2$ with 2 equiv of lithium phenylacetylide in THF for a short time (5 min) produced the mixed ligand complex **1**, $[Co_3(dpa)_4(CCPh)(NCCH_3)](PF_6)$, though the yield was low. Nevertheless, the formation and isolation of **1** is significant because it shows that substitution of the axial ligands under these conditions may be controlled to take place one step at a time.

In a study of the influence of various reaction conditions, it was found that a change of reaction solvent from THF to acetonitrile has a dramatic impact on the outcome of the reaction. Upon addition of lithium phenylacetylide to an acetonitrile solution of the relevant $[M_3(dpa)_4(NCCH_3)_2](PF_6)_2$ species, the $M_3(dpa)_4(CCPh)_2$ complexes of chromium, **2**, cobalt, **3**, and nickel, **4**, precipitate from the reaction mixture as indicated in eq 3.

$$[M_3(dpa)_4(NCCH_3)_2](PF_6)_2 + \text{excess LiCCPh} \rightarrow M_3(dpa)_4(CCPh)_2 \quad (3)$$

These compounds can thus be obtained in useful yields of 40−60% after recrystallization from mixtures of benzene− or toluene−hexanes. Moreover, no chloride ions were detected in the crystal structures, and the compounds are analytically pure.

Crystal Structures. The previously reported structure of “$Cr_3(dpa)_4(C{\equiv}CPh)_2$”[17] was re-refined using a similar model to those described previously for analogous trinickel compounds having disordered axial ligands (partially occupied phenylacetylide and chloride ligands).[19] The thermal ellipsoids of the phenylacetylide ligands in the previously reported structure are anomalous: The ellipsoids for the carbon atoms bonded to the Cr atoms are unusually small, indicative of a greater amount of electron density near those positions than can be accounted for by only carbon atoms. Thus, chloride ions were placed near these carbon atoms, and refinement was resumed with a model in which the relative occupancies of phenylacetylide ligands and chloride ligands were refined with the constraint that their sum should equal 1 for each axial site. During the refinement, the chloride ions moved to a distance of 2.49 Å from the chromium atoms, which is a reasonable Cr−Cl distance (as compared to those in $Cr_3(dpa)_4Cl_2$, which are 2.51−2.56 Å), and the thermal parameters for the axial ligands look much more reasonable. After the re-refinement, the formula of the molecule is best represented as $Cr_3(dpa)_4(C{\equiv}CPh)_{1.8}Cl_{0.2}$. Plots of the structure as reported previously[17] and also as reinterpreted here are shown in Figure 1.

Crystal data are shown in Table 1, and relevant bond distances for **1**−**4** are given in Table 2. Compounds **1**−**4** crystallize in centrosymmetric space groups, but in each case the molecule resides on a general position. There are two M−M distances for each compound that are not required to be the same. For **1** (Figure 2), the Co−Co distances are both 2.328(1) Å, despite there being two different axial ligands. In contrast, **3** is unsymmetrical (Figure 3), despite having two equivalent axial ligands. The unsymmetrical Co−Co distances of 2.344(1) and 2.401(1) Å suggest the presence of a diamagnetic Co_2^{4+} unit and a paramagnetic Co(II) center. This assignment is supported further by the longer Co−N bond distances for the latter.

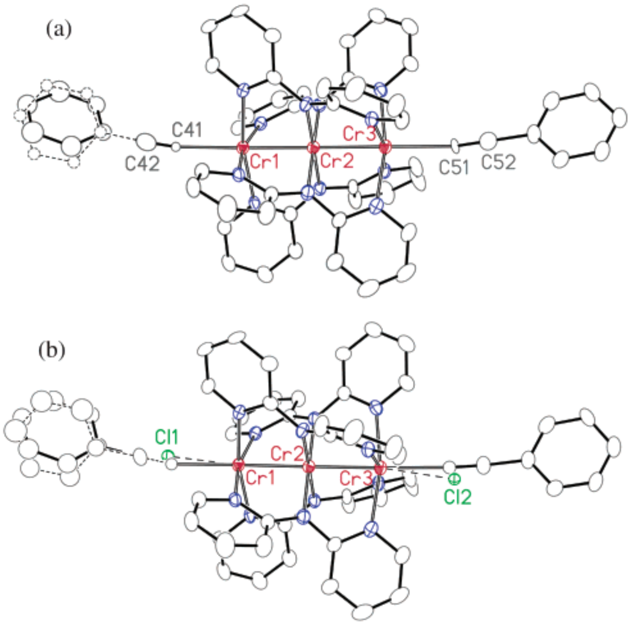

Figure 1. Thermal ellipsoid plot of “$Cr_3(dpa)_4(CCPh)_2$” (a) as reported in ref 17 and (b) as reinterpreted here with the formula $Cr_3(dpa)_4(CCPh)_{1.8}Cl_{0.2}$. The unusually shaped ellipsoids for C41, C42, C51, and C52 in part (a) indicate the presence of chloride impurities. Ellipsoids are drawn at 30% probability, and hydrogen atoms have been removed.

It is well-known that the $Cr_3(dpa)_4^{2+}$ core has a strong tendency to crystallize with unsymmetrical Cr_3^{6+} chains consisting of one diamagnetic Cr_2^{4+} quadruple bond and one isolated high-spin Cr(II) ion.[17] However, in **2**, (shown in Figure 4) the Cr−Cr distances of 2.427(2) and 2.429(2) Å are effectively identical. Furthermore, the Cr−C bond distances, 2.241[7] Å, are nearly as long as those, 2.284(2) Å, in the rigorously symmetrical $Cr_3(dpa)_4(CN)_2$.[16c] The molecular structure of **4** has already been reported, but in this work the molecule has been obtained in a new crystal form, namely, **4**•2.1benzene•0.5 hexane. The structure (shown in Figure S1) is the same as the previously reported one within experimental error,[16b] having two terminal high-spin Ni^{2+} ions and a central square planar diamagnetic Ni^{2+} ion. The Ni•••Ni distances, 2.466(1) and 2.481(1) Å, while different in a statistically significant sense, are equal from a chemical point of view.

Spectroscopy. Compounds **1**−**4** were all detected by mass spectrometry, showing either a molecular ion (for **2** and **3**) or the parent molecule minus one axial ligand (**1** and **4**). The IR spectra of **2**−**4** show distinct C≡C stretching bands between 2000 and 2100 cm^{-1} which appear to decrease in energy across the series Ni > Co > Cr. This is consistent with back-bonding from the M_3 π orbitals to the C≡C π^* orbitals, as observed in quadruply bonded Mo_2^{4+} species with bonds to alkynyl groups.[20] Also, in phenylacetylide com-

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[19] Crystal data for $Cr_3(dpa)_4(CCPh)_{1.8}Cl_{0.2}$: monoclinic, $P2_1/c$, a = 16.849(5) Å, b = 15.460(7) Å, c = 20.479(3) Å, β = 110.96(3)°, d = 1.385 g cm^{-3}, μ = 0.694 mm^{-1}, R1 ($I > 2\sigma(I)$) = 0.0685, wR2 ($I > 2\sigma(I)$) = 0.1624, R1 (all data) = 0.0971, wR2 (all data) = 0.1874.

Table 1. Crystal Data[a]

	$[Co_3(dpa)_4(NCCH_3)(CCPh)](PF_6)\cdot 4THF$ **1**·4THF	$Cr_3(dpa)_4(CCPh)_2$ **2**	$Co_3(dpa)_4(CCPh)_2$ **3**	$Ni_3(dpa)_4(CCPh)_2\cdot$2.1benzene·0.5hexane **4**·2.1benzene·0.5hexane
formula	$C_{65.8}H_{71.6}Co_3F_6N_{13}O_{3.95}P$	$C_{56}H_{42}N_{12}Cr_3$	$C_{56}H_{42}N_{12}Co_3$	$C_{71.20}H_{60.90}N_{12}Ni_3$
fw	1429.52	1039.02	1059.81	1260.72
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	15.409(3)	16.86(1)	16.707(4)	16.241(1)
b, Å	16.297(3)	15.35(1)	15.434(4)	23.643(2)
c, Å	16.340(3)	20.37(1)	20.000(5)	17.177(1)
α, deg	73.289(4)	90	90	90
β, deg	65.744(4)	110.91(1)	111.204(4)	96.635(1)
γ, deg	77.236(4)	90	90	90
V, Å^3	3558(1)	4924(5)	4808(2)	6551.3(8)
Z	2	4	4	4
d(calcd), g cm^{-3}	1.344	1.402	1.464	1.278
R1,[b] wR2[c] ($I > 2\sigma I$)	0.0641, 0.1519	0.0572, 0.1480	0.0459, 0.1078	0.0767, 0.1766
R1,[b] wR2[c] (all data)	0.1200, 0.1756	0.1298, 0.1864	0.0960, 0.1298	0.1015, 0.1898

[a] In compounds with partially occupied solvent molecules in the crystals, the occupancies of these solvent molecules have been rounded up to the nearest decimal place. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table 2. Selected Bond Distances (Å) for **1**−**4**

	1·4THF	**2**	**3**	**4**·2.1benzene·0.5hexane
M1−M2	2.328(1)	2.427(2)	2.344(1)	2.466(1)
M2−M3	2.328(1)	2.429(2)	2.401(1)	2.481(1)
M1−N	1.990[6]	2.123[5]	1.980[4]	2.106[5]
M2−N	1.901[6]	2.030[5]	1.911[4]	1.900[5]
M3−N	1.982[6]	2.120[5]	2.025[4]	2.105[5]
M−C	2.034(8)	2.241[7]	2.022[5]	2.022[7]
$M-N_{ax}$	2.114(6)			
C≡C	1.193(9)	1.188[8]	1.196[8]	1.177[9]
N≡C	1.114(8)			

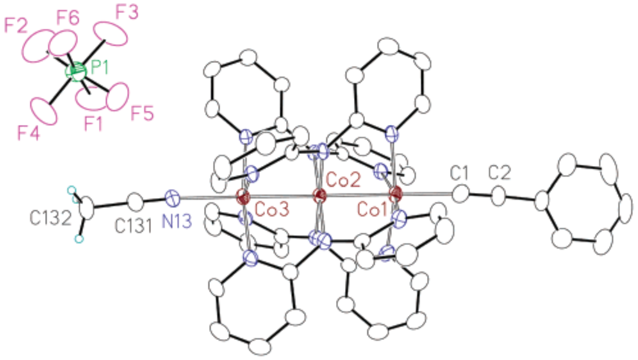

Figure 2. Plot of **1** with ellipsoids drawn at the 30% probability level. Aryl H atoms and interstitial solvent molecules have been removed.

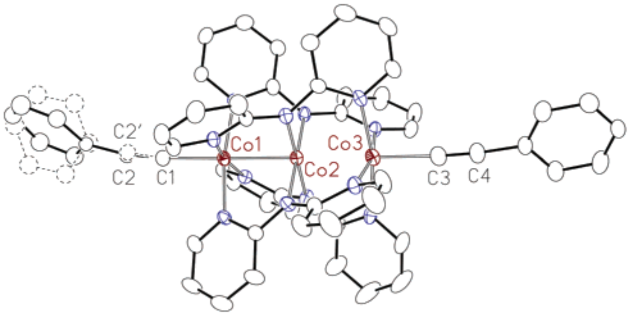

Figure 3. Plot of **3** with thermal ellipsoids drawn at the 30% probability level.

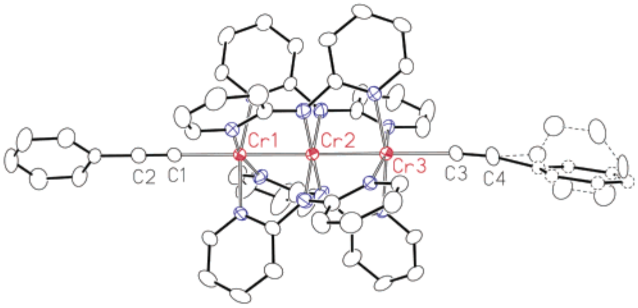

Figure 4. Thermal ellipsoid plot of **2** with hydrogen atoms removed and ellispoids drawn at the 30% probability level.

plexes having Ru_2^{6+} units with formamidinate bridging ligands, **III**,[21,22] the C≡C stretching frequencies are in the narrow range 2099−2102 cm^{-1}, and $Ru_2(DMBA)_4(CCPh)_2$ (DMBA = dimethylbenzamidinate) has a somewhat lower band at 2080 cm^{-1} which is nearly identical to the position of the C≡C stretching frequency of **4** (2081 cm^{-1}).

Although **3** is unsymmetrical in the solid state, solutions show no characteristics of asymmetry. The ^{1}H NMR spectrum shows four resonances at 50.52, 38.95 (d), 16.05 (d), and 12.40 ppm which can be assigned, as previously,[23] to the pyridyl protons. These signals are characteristically shifted from their normal positions due to the paramagnetism of the Co_3^{6+} unit but are consistent with D_4 symmetry for the $Co_3(dpa)_4^{2+}$ core. Less shifted are the aromatic phenylacetylide resonances at 6.89 (t), 5.22 (t), and 2.35 (d) ppm which appear in a 2:1:2 intensity ratio, consistent with the two phenyl groups being equivalent. Solutions of **3** show an absorption in the visible region at 587 nm (ϵ = 2000 M^{-1} cm^{-1}), near where similar peaks appear for solutions of all other Co_3^{6+} complexes,[16a] regardless of whether they are symmetrical or unsymmetrical in the solid state.

Electrochemistry. The contributions of the acetylide ligands to the trimetal molecular orbitals have a significant effect on the redox potentials of **2**−**4** in THF solution (see

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Table 3. Electrochemical Results for **2**−**4**

	$(E_{1/2})_1$,[a] V	$(E_{1/2})_2$,[a] V
2	−0.465	0.795
	(0.063)[b]	(0.846)[b]
	(0.528)[c]	(0.051)[c]
3	0.121	0.725
	(0.320)[b]	(1.24)[b]
	(0.199)[c]	(0.525)[c]
4	0.860	NA
	(0.908)[b]	
	(0.048)[c]	

[a] THF solution, NBu_4PF_6 electrolyte, Pt disk working electrode, Pt wire auxiliary electrode, Ag/AgCl reference electrode, scan rate of 100 mV/s. [b] These values are for the corresponding $M_3(dpa)_4Cl_2$ species in CH_2Cl_2 solution. [c] The difference between the corresponding $E_{1/2}$ of the $M_3(dpa)_4Cl_2$ and $M_3(dpa)_4(CCPh)_2$ species.

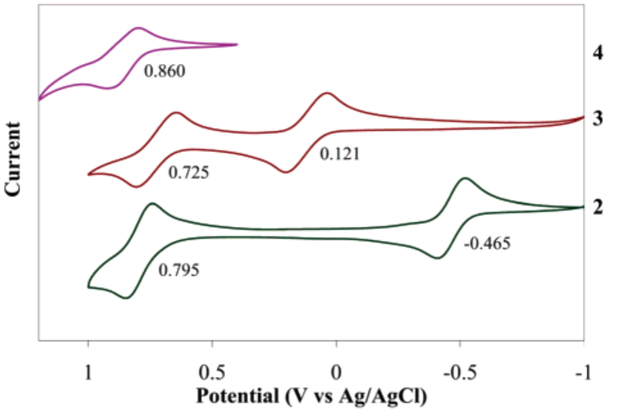

Figure 5. Cyclic voltammograms (in THF taken in the clockwise direction) of **2**−**4** with $E_{1/2}$ values labeled.

Table 3 and Figure 5), and they are here compared to the redox potentials of the analogous $M_3(dpa)_4Cl_2$ complexes. The first oxidation potential of −0.465 V for the Cr compound is particularly low, as is the second oxidation potential of 0.725 V for **3**; both values are both over 0.5 V more accessible than the corresponding processes in $Cr_3(dpa)_4Cl_2$ and $Co_3(dpa)_4Cl_2$. The first oxidation potential for **3** at 0.121 V is lower than that in $Co_3(dpa)_4Cl_2$ by 0.199 V. The other redox waves for these compounds occur at slightly lower potentials, but it should be emphasized that the oxidations are more accessible for **2**−**4** than for any of the corresponding $M_3(dpa)_4X_2$ species, or even for the $M_3(depa)_4X_2$ complexes of the diethyl-substituted dpa (depa) ligand.

Thus far, no oxidation products have been isolated, and in order to isolate such products, the reaction conditions must be carefully chosen. Compounds **2**−**4** are unstable in chlorinated solvents, as evidenced from their cyclic voltammograms taken in CH_2Cl_2 solution. For all three complexes, small waves which became more intense over time appeared near the main peaks in the positions of the corresponding $M_3(dpa)_4Cl_2$ species. Thus, it seems that **2**−**4** react with chlorinated solvents as shown in eq 4.[24]

$$M_3(dpa)_4(CCPh)_2 \xrightarrow{CH_2Cl_2} M_3(dpa)_4Cl_2 + \text{organic products} \quad (4)$$

Compound **2** is also unstable in THF (though **3** and **4** are stable), decomposing with loss of one Cr atom yielding $Cr_2(dpa)_4$, which crystallizes out of such solutions. This probably explains why the second oxidation wave for **2** shown in Figure 5 has larger peak currents than the first wave, since the solution must contain a small but significant amount of $Cr_2(dpa)_4$, whose $Cr_2^{4+/5+}$ redox wave occurs near the $Cr_3^{7+/8+}$ wave for **2**.

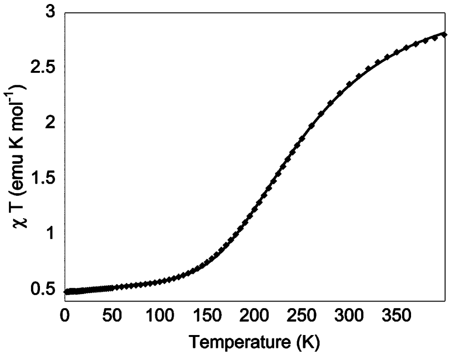

Figure 6. Plot of χT vs T for **3**. The solid line represent a least-squares fitting of the data.

Magnetic Susceptibilities of 2 and 3. The magnetic properties of the new phenylacetylide complexes are similar to those of the corresponding chloro complexes. For compound **2**, $\chi T = 2.8$ emu K mol^{-1} at 300 K. However, it decreases steadily as the temperature is lowered, and below 20 K there is a steeper decrease. A plot of $1/\chi$ versus T can be fit to the Curie−Weiss equation for $S = {}^1/_2$, yielding a g value of 1.924(2) and a Weiss constant of −3.2(2) K. The decrease in χT at low temperatures and thus the comparatively large Weiss constant can be attributed to zero-field splitting of the quintet ground state.

Like other previously reported Co_3^{6+} EMACs,[9,25] compound **3** exhibits spin crossover behavior, as shown by the sigmoidal χT versus T curve shown in Figure 6. At low temperatures (<100 K), the data approach a value of $\chi T = 0.5$ emu K mol^{-1} indicating $S = {}^1/_2$, while at high temperatures, χT reaches a value of 2.8 emu K mol^{-1}. The curve was modeled using methods which we have described previously.[25] The g values for the high-spin ($S = {}^3/_2$) and low-spin ($S = {}^1/_2$) states refine to 2.257(3) and 2.651(6), respectively. Values much higher than the spin-only values would require large orbital contributions to the magnetic susceptibility. There is also a large temperature-independent paramagnetism contribution to the low-spin state. The thermodynamic quantities associated with the $S = {}^1/_2 \rightarrow S = {}^3/_2$ spin equilibrium are $\Delta H = 9.05(8)$ kJ/mol, $\Delta S = 34.4(1)$ J K^{-1} mol^{-1}, and $T_c = \Delta H/\Delta S = 263.7(8)$ K, which are similar in magnitude to those found for $Co_3(depa)_4Cl_2$,[25] which are $\Delta H = 6.0(2)$ kJ mol^{-1}, $\Delta S = 28(2)$ J K^{-1} mol^{-1}, and $T_c = 214(7)$ K. Since the analogous chloro compound, $Co_3(dpa)_4Cl_2$, also shows spin crossover behavior but the high-spin state does not saturate at higher temperatures, it must be concluded that the acetylide ions in **3** stabilize this

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(24) The ability of such chlorinated solvents to act as chloride donors and often as oxidizing agents is well-known in coordination chemistry. For example, see: Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Timmons, D. J.; Wilkinson, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 9249.

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$S = {}^{3}/_{2}$ state. The magnetic data for **4** have been discussed previously.[16b]

Conclusions

Complexes **2**−**4** are stable as solids, thus suggesting that it may be feasible to incorporate the trimetal units into polyynyl chains to be used in molecule scale devices. The trinickel complexes exist with two unpaired electrons on each terminal Ni^{II} ion and a diamagnetic square planar central Ni atom, though oxidation of $Ni_3(dpa)_4Cl_2$ has been shown to result in delocalized three-center Ni−Ni bonding in the Ni_3^{7+} products.[13d] Also, though the Cr_3^{6+} chain in **2** is symmetrical with respect to the Cr−Cr distances (and thus a delocalized electronic structure is expected), all known Cr_3^{7+} species are known to have unsymmetrical trichromium chains having a diamagnetic Cr_2^{4+} quadruple bond and an isolated high-spin Cr^{III} ion.[26] Thus, the $Ni_3^{6+/7+}$ and $Cr_3^{6+/7+}$ units can be used as molecular switches, since their electronic structure changes drastically upon oxidation;[13d] Co_3^{6+} species, which have two accessible spin states, have the potential for utilization in magnetic data storage devices. The formation of **1** shows that the introduction of axial alkynyl ligands under these conditions can be carried out in a stepwise manner, so that it will be possible to synthesize compounds containing two different types of acetylide ions. Attempts to capitalize on this are underway with the goal of producing complexes with different end caps in which electronic communication from one end to the other may be observable. Thus, the chemistry reported here opens a path for the synthesis of new molecular devices and interesting novel materials incorporating trimetal units.

Experimental Section

General. All manipulations were carried out under an atmosphere of dry nitrogen gas using standard Schlenk techniques. Toluene, THF, and hexanes were purified by means of a Glass Contour solvent system. Other solvents were distilled in a nitrogen atmosphere over appropriate drying agents prior to use. $Cr_3(dpa)_4(NCCH_3)_2(PF_6)_2$,[16c] $Co_3(dpa)_4(NCMe)_2(PF_6)_2$,[27] and $Ni_3(dpa)_4(NCCH_3)_2(PF_6)_2$[28] were prepared according to previously reported methods. IR spectra were taken on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. Cyclic voltammograms were taken on a CH Instruments electrochemical analyzer using 1 M NBu_4PF_6 solutions in THF. The electrodes were the following: Pt disk (working), Pt wire (auxiliary), and Ag/AgCl (reference). ^1H NMR spectra were obtained on a VXR-300 NMR spectrometer. Mass spectrometry data (electrospray ionization) were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University, using an MDS Series Qstar Pulsar with a spray voltage of 5 keV. UV−vis−NIR spectra were obtained on a Cary 17 spectrophotometer. Elemental analyses were carried out by Canadian Microanalytical Services in British Columbia, Canada.

Synthesis of $[Co_3(dpa)_4(CCPh)(NCCH_3)](PF_6)$, 1. To a small Schlenk flask containing 10 mL of THF was added 40 μL (0.32 mmol) of phenylacetylene. The colorless solution was cooled in an ice water bath, and 200 μL of a 1.6 M solution of methyllithium in diethyl ether was slowly added. The solution was allowed to warm to room temperature and then stirred for ∼$^1/_2$ h during which time it became pale yellow. This solution was transferred via cannula to a suspension of 158 mg (0.128 mmol) of $[Co_3(dpa)_4(NCCH_3)_2](PF_6)_2$ in 10 mL of THF. The mixture became dark yellow/black and was stirred for 5 min. Then, 15 mL of hexanes was added with stirring, resulting in some dark precipitate. The mixture was filtered, and the filtrate was left in the freezer at −40 °C for 3 months. Some small crystals grew which have the composition $[Co_3(dpa)_4(CCPh)(NCCH_3)](PF_6)\cdot 4THF$. IR (KBr, cm^{-1}): 3447 br, m, 3069 w, 3025 w, 2963 w, 2066 w, 1654 w, 1637 w, 1602 s, 1592 s, 1545 w, 1466 vs, 1369 s, 1312 m, 1281 w, 1262 w, 1200 w, 1154 w, 1102 w, 1053 w, 1019 m, 840 m, br, 758 m, 695 w, 558 w, 519 w, 461 w, 429 w. ESI+ mass spectrum (*m/z*): 958 $(M - NCCH_3 - PF_6)^+$.

General Synthesis of $M_3(dpa)_4(CCPh)_2$ (M = Cr, Co, Ni for 2, 3, and 4, Respectively). A solution of 80 μL (0.64 mmol) of phenylacetylene in 5 mL of THF was cooled to 0 °C by means of an ice water bath. A 400 μL solution of 1.6 M MeLi in Et_2O was carefully added. This solution was stirred for $^1/_2$ h as it was allowed to warm to room temperature, and then it was added via cannula to another flask containing 0.128 mmol of the corresponding $[M_3(dpa)_4(NCCH_3)_2](PF_6)_2$ complex dissolved in 20 mL of acetonitrile. After stirring the resulting dark mixture for $^1/_2$ h, a fine precipitate formed and was collected by filtration. The solid was washed with Et_2O (3 × 15 mL) (washed with MeCN in the case of **4**), dissolved in 15 mL of toluene (or benzene), and filtered, and the extract was layered with hexanes. Crystals grew over the course of a week. For **2**, yield: dark brown crystals, 63%. IR (KBr, cm^{-1}): 3447 m, br, 3066 w, 3023 w, 2963 w, 2044 w, 1594 s, 1545 w, 1465 vs, 1426 vs, 1365 m, 1310 m, 1262 m, 1153 m, 1096 s, br, 1015 m, 803 m, 766 m, 681 w, 643 w, 472 m, 437 w. ESI+ mass spectrum (*m/z*): 1038 M+. Anal. calcd for $Cr_3C_{62}H_{54}N_{12}O_3$: C 63.58, H 4.65, N 14.35%. Found: C 63.11, 4.60, 14.49%. Vis (C_6H_6 solution; λ, nm (ϵ, M^{-1} cm^{-1})): 691 (1000), 625 (1000), 539 (2000). For **3**, yield: dark brown crystals, 41%. IR (KBr, cm^{-1}): 3069 w, 3022 w, 2068 w, 1603 s, 1591 s, 1546 w, 1465 vs, 1456 vs, 1424 vs, 1369 s, 1312 m, 1281 w, 1199 w, 1152 m, 1018 w, 1007 w, 882 m, 756 m, 738 w, 694 w, 541 w, 520 w, 464 w, 428 w. ESI+ mass spectrum (*m/z*): 1059 M+. Anal. calcd for $Co_3C_{56}H_{44}N_{12}O_1$: C 62.40, H 4.11, N 15.59%. Found: C 62.92, H 4.10, N 15.68%. UV−vis−NIR (THF solution; λ, nm (ϵ, M^{-1} cm^{-1})): 1220 (100), 747 (400), 587 (2000), 482 (sh, 5000), 425 (sh, 20 000), 329 (100 000), 278 (100 000). For **4**, yield: dark red-purple crystals, 60%. Vis (C_6H_6 solution; λ, nm (ϵ, M^{-1} cm^{-1})): 591 (1000), 500 (3000). Other characterization has been reported.[16b]

Compound **2** is very difficult to handle in solution, and it is also difficult to crystallize. While it is stable in solvents such as benzene and toluene, the crystal structures of $\mathbf{2}\cdot xC_6H_6$ or $\mathbf{2}\cdot xC_7H_8$ (which are isomorphous) could not be successfully solved since the systematic absences are not consistent with any known space group. Compound **2** is also soluble in THF, but it decomposes to $Cr_2(dpa)_4$ at room temperature, and also at low temperatures. In other solvents, **2** is either unstable or not very soluble. Crystals of **2** from which the structure reported here was solved were grown by setting aside the reaction mixture described above without stirring.

X-ray Crystallography. In each case a suitable crystal was mounted on the end of a quartz fiber by a small amount of grease and transferred to the goniometer of a Bruker SMART 1000 CCD area detector system where it was cooled to −60 °C for the duration of the experiment. Initial unit cell parameters were obtained from SMART[29] software. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by

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(27) Clérac, R.; Cotton, F. A.; Dunbar, K. R.; Lu, T.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2000**, *39*, 3065.

SAINTPLUS.[30] The data were further corrected for absorption by SADABS.[31] The initial structure solutions were obtained by the direct methods routine in SHELXTL.[32] Subsequent refinement cycles (based on F^2) and Fourier synthesis revealed the positions of all the non-hydrogen atoms. These atoms (with the exception of disordered groups) were refined using anisotropic displacement tensors. All hydrogen atoms were added in calculated positions for the final refinement cycle. The previously reported[17] structure of $Cr_3(dpa)_4(CCPh)_2$ was re-refined using data from our archives and without further manipulation.

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Supporting Information Available: Thermal ellipsoid plot of **4** and crystal data in CIF format for **1**−**4** and the re-refined structure of $Cr_3(dpa)_4(CCPh)_{1.8}Cl_{0.2}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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