

Preparation of an Isocyano- β -diketone via its Metal Complexes, by Use of Metal Ions as Protecting Groups

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A ligand containing isocyanide and β -diketone functional groups, 3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC), and several of its metal complexes have been prepared. The free isocyano- β -diketone could not be prepared by dehydration of the analogous formamide, HacphNHCHO, because of the reactivity of its β -diketone moiety. Instead, the metal complexes Al(acphNC)₃, Fe(acphNC)₃, Cu(acphNC)₂, and Zn(acphNC)₂ were synthesized by dehydration of the formamido- β -diketonate complexes Al(acphNHCHO)₃, Fe(acphNHCHO)₃, Cu(acphNHCHO)₂, and Zn(acphNHCHO)₂. The free isocyano- β -diketone, HacphNC, can be liberated from its Al and Fe complexes by treatment with oxalate (C₂O₄²⁻) and HC₂O₄⁻. In addition to these O-bound complexes, C(N)-bound complexes can be prepared by the reaction of either Al(acphNC)₃ or HacphNC with Au(I). X-ray analyses of HacphNC, Al(acphNC)₃, (HacphNC)AuCl, Cu(acphNHCHO)₂, *trans*-Zn(acphNHCHO)₂(H₂O)₂, and two other intermediates are also reported.

Introduction

Heterofunctional ligands are of interest because of their ability to bind to different types of metal ions. This is important in the construction of metal–organic frameworks (MOFs). MOFs have attracted scientists because the various coordination geometries and abilities of metal ions together with different types of ligands provide many possible open framework structures. Rational design of ligands can lead to predictable extended solid frameworks with potential applications in separation, gas storage, molecular recognition, and catalysis.^{1–5}

Several porous frameworks have been prepared from the heterofunctional ligand pyridylacetylacetone (pyacH) by Domasevitch et al.^{6,7} and by our group.^{8,9} For example, a

porous 1D ladder structure prepared from Fe(pyac)₃ and AgNO₃ is of interest because the solvent guests in its pores can be exchanged in single-crystal-to-single-crystal transformations.⁹

Although the above 1D Fe(pyac)₃–AgNO₃ porous framework is stable under solvent exchange, the others are not, and all are unstable in a vacuum. This limited stability is likely due to the weakness of the interactions between layers in these networks. Our goal is to develop ligands that are suitable for the construction of porous 3D frameworks, because they are expected to show greatly enhanced stability. The most promising route to 3D structures is to use conditions that favor the assembly of six ligands coordinated octahedrally around one metal. Although a few M(py)₆ⁿ⁺ complexes are known, they generally form only in the presence of excess pyridine.^{10–12} Thus, pyridine-based ligands, such as pyac⁻, are unlikely to be useful in preparing 3D supramolecular materials. One common method for stabilizing metal complexes is choosing chelating ligands. However, in our case, a chelating ligand (e.g., a 2,2-bipyridine derivative) is difficult to functionalize so that it will also bind to two other metal atoms. Therefore, in order to improve the prospects for 3D materials, we need to use building blocks based on strongly coordinating monodentate ligands. Nitriles, such as 3-(4-cyanophenyl)acetylacetone, have been studied as

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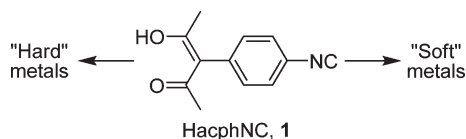


Figure 1. The bifunctional isocyano- β -diketone HacphNC.

heterofunctional ligands,¹³ but nitriles tend to bind weakly to metals, making it difficult to generate six-coordinate complexes $M(NCR)_6^{n+}$. On the other hand, isocyanide ligands (CNR) are known to make stable complexes $M(CNR)_6^{n+}$ with metals such as Cr,^{14–20} Mn,^{21–26} Fe,^{27–29} and Re.^{30–34} Early on, Sacco and Naldini synthesized highly stable manganese(I) isocyanide complexes $[(RNC)_6Mn]^+$.^{21–23} More recently, Barybin et al. have prepared a number of homoleptic isocyanide complexes (e.g., $Cr(CNfC)_6$ (Fc = ferrocenyl)¹⁹) in high yield, using only a slight excess of the isocyanide ligand.

We were interested in HacphNC (1, Figure 1), with one isocyanide and one β -diketone moiety, for possible conversion to 3D porous materials. This ligand's isocyanide moiety should be able to bind to "soft" metals such as Cr(0), Mn(I), or Fe(II) and its β -diketone moiety to "hard" metals such as Cu(II) or Zn(II). We report here the preparation of the HacphNC ligand and the properties of several of its metal complexes.

Results and Discussion

Synthetic Strategy. Figure 2 illustrates the overall route we chose for synthesizing the target compound, HacphNC (1), via 3-(4-formamidophenyl)acetylacetone (HacphNHCHO, 2), from 4-nitrobenzaldehyde (3). Reduction of the nitro group of 3 and formylation of the resulting amine, and conversion of its aldehyde to a

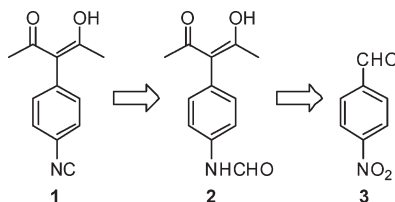


Figure 2. Synthetic strategy for the isocyano- β -diketone HacphNC (1).

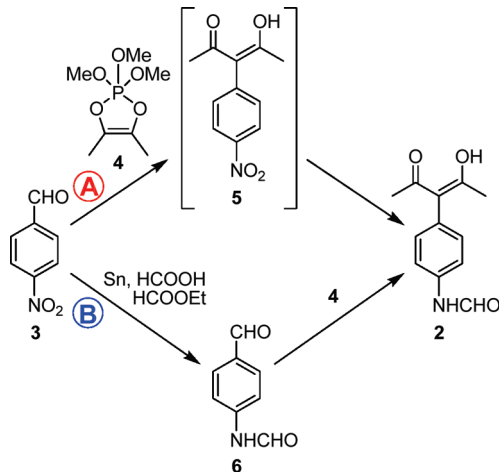


Figure 3. Two possible routes for preparing HacphNHCHO (2).

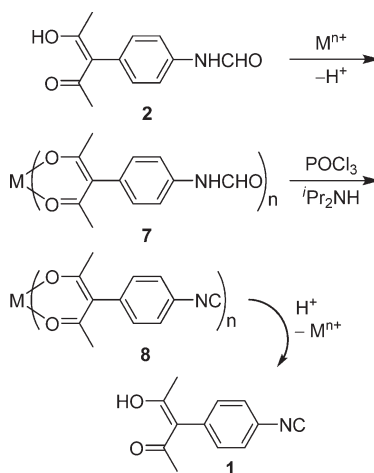


Figure 4. Protection of the β -diketone group by coordination to metal ions prior to isocyanide synthesis.

β -diketone, was expected to yield 2. Isocyanides are normally prepared by dehydration of formamides; thus, dehydration of 2 was expected to produce 1.

We tested two possible routes starting from 4-nitrobenzaldehyde (3) to make 2 (Figure 3). In route A, the aldehyde group is converted into a β -diketone first (making 5), and then the nitro group is reduced to an amino group and formylated. In route B, the nitro group is reduced to an amino group and formylated first (6), and then the aldehyde is converted into a β -diketone.

After the aldehyde group is converted into a β -diketone, it is coordinated to metal ions, which serve as a "protecting group" (Figure 4). The metal formamido- β -diketonate complex 7 can then be dehydrated to an isocyanide complex (8). Free HacphNC (1) can be liberated

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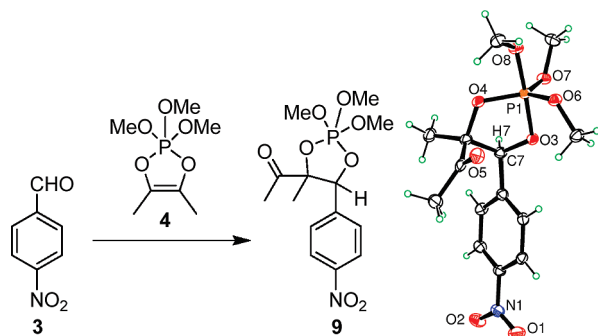


Figure 5. Synthesis and ellipsoid plot of (4-nitrophenyl)phospholane intermediate **9**.

by treatment of the metal isocyano- β -diketonate complex with a suitable metal-complexing agent or with dilute acid.

Synthesis of HacphNHCHO (2). We attempted to prepare 3-(4-nitrophenyl)acetylacetone (**5**) by route A. 4-Nitrobenzaldehyde (**3**) was mixed with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene (**4**) in dichloromethane for one day, and then the mixture was refluxed in anhydrous methanol for three days. (The conversion of aromatic aldehydes to 3-arylacetylacetones by reaction with **4** was first explored by Ramirez et al.³⁵) The first stage of this reaction proceeds cleanly, producing **9** (4-acetyl-4-methyl-5-(4-nitrophenyl)-2,2,2-trimethoxy-1,3,2-dioxaphospholane; Figure 5). We identified **9** by NMR spectroscopy and by X-ray analysis (see the Supporting Information). However, our attempts to convert **9** to the desired (4-nitrophenyl)acetylacetone **5**, under several different conditions, were unsuccessful. (This may be due to the electron-withdrawing effect of the nitro group in **9**.)

Because route A was not successful (see Figure 3), we turned to route B for the synthesis of **2**. Conversion of **3** to **6** proceeds by initial reduction to produce 4-aminobenzaldehyde, followed by rapid formylation to make **6**. The intermediate 4-aminobenzaldehyde self-condenses to yield insoluble polymeric products; thus, it should be formylated as quickly as possible to give a good yield of 4-formamidobenzaldehyde (**6**). Hrvatin and Sykes³⁶ reported the conversion of **3** to **6** using tin metal and formic acid in toluene. We modified their procedure by replacing toluene (as solvent) with a mixture of ethyl formate and ethyl acetate, increasing the amount of formic acid, and adding the tin metal in smaller portions. Our modifications in the procedure were designed to keep all of the liquid components of the reaction mixture miscible, generate 4-aminobenzaldehyde more slowly, and formylate it faster to make **6**; the resulting yield was higher (66%, vs lit.³⁶ 47%).

Compound **6** reacts with phospholene **4** in dichloromethane to generate β -diketone **2** (HacphNHCHO, Figure 3), which was purified by column chromatography and isolated as yellow crystals. Both *E* and *Z* forms of **2** and **6** were characterized (see the Supporting Information). The new β -diketone **2** also exhibits keto–enol

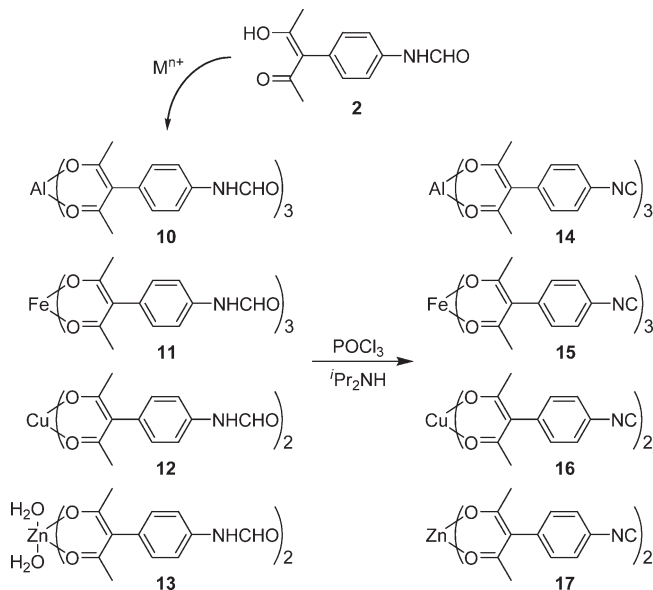


Figure 6. Preparation of formamido- β -diketonate complexes **10–13** and their conversion to isocyano- β -diketonate complexes **14–17**.

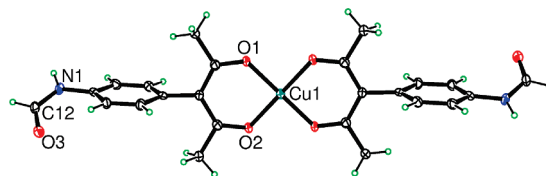


Figure 7. Crystal structure of Cu(Z-acphNHCHO)₂ (**12**).

tautomerism (in CDCl₃, 94% enol: 6% keto by ¹H NMR).

Syntheses of M(acphNHCHO)_n. The β -diketone moiety of **2** required protection before dehydration of the formamido group to an isocyanide. (Attempts to prepare **1** directly by the dehydration of **2** were unsuccessful; see below.) We chose metal ions as “protecting groups” for the β -diketone because there are numerous procedures available for preparing metal β -diketonates. Also, dehydration of the resulting metal formamido- β -diketonates (M(acphNHCHO)_n) should yield metal isocyano- β -diketonates (M(acphNC)_n), which may be useful in building supramolecular structures even without isolation of free HacphNC (**1**). We chose the metal ions Al³⁺, Fe³⁺, Cu²⁺, and Zn²⁺, to react with **2** (Figure 6).

We prepared Al(acphNHCHO)₃ (**10**) and Fe(acphNHCHO)₃ (**11**) by the reaction of Al(NO₃)₃ and Fe(NO₃)₃, respectively, with HacphNHCHO (**2**) in the presence of NaHCO₃. This is similar to previously published procedures for Al(pyac)₃ and Fe(pyac)₃.^{7,9,37} The products are soluble in DMSO and acetone, and slightly soluble in chloroform and dichloromethane.

Bluish-green Cu(acphNHCHO)₂ (**12**) precipitates immediately when **2** and copper(II) acetate are mixed together in water/methanol solution. Compound **12** (see Figure 7) is slightly soluble in DMSO and soluble in pyridine, but insoluble in almost all other common

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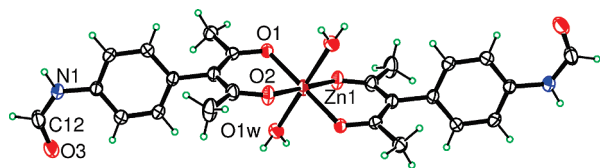


Figure 8. Ellipsoid plot of *trans*-Zn(Z-acphNHCHO)₂(H₂O)₂ (**13**), from the crystal structure of its dihydrate.

solvents. The structure of **12** also contains intermolecular contacts (Cu1···O3, 2.838(2) Å), which make the structure polymeric and give the Cu atoms an approximately octahedral coordination geometry overall.

trans-Zn(acphNHCHO)₂(H₂O)₂ (**13**) is made from zinc acetate and **2**, with added NaHCO₃. Crystals grown during the synthesis were suitable for single-crystal X-ray analysis. In the structure of **13** (see Figure 8), the two β -diketonate groups form a stepped arrangement about Zn²⁺. This contrasts with the structure of **12**, in which the two acac moieties are coplanar. Compound **13** is readily soluble in DMSO and pyridine, and slightly soluble in chloroform and dichloromethane.

M(acphNC)_n Complexes. All four metal formamido- β -diketonate complexes (**10**–**13**) can be dehydrated by POCl₃ in the presence of diisopropylamine (Figure 6), in a dichloromethane solution. The starting materials are not very soluble in CH₂Cl₂, whereas the products dissolve readily. The Al, Fe, and Zn starting materials (**10**, **11**, and **13**) all react within 2 h. In contrast, most of the copper starting material (**12**) still remains as unreacted solid even after five days. This slow reaction may be due to the fact that **12** is polymeric in the solid state (see Figure 7). Such polymerization would explain the low solubility of **12** and also interfere sterically with the dehydration reaction. A similar phenomenon is observed with Cu(pyac)₂: its crystals are also polymeric, which leads to low solubility in a variety of solvents.³⁸

The IR absorptions ($\nu_{\text{C}\equiv\text{N}}$) for the isocyano- β -diketonate complexes Al(acphNC)₃ (**14**), Fe(acphNC)₃ (**15**), Cu(acphNC)₂ (**16**), and Zn(acphNC)₂ (**17**) appear at 2121, 2126, 2147, and 2124 cm⁻¹, respectively. The values for **14**, **15**, and **17** are very close to those for free aryl isocyanide ligands^{39–42} and for the free ligand HacphNC (2122 cm⁻¹; see below). The higher frequency for the Cu complex (**16**) may again indicate coordination of the isocyanide groups to adjacent Cu atoms, but it could be obtained only in impure form. The yield for **17** was low (13%); this may be due to the fact that the Zn complex reactant, **13**, was hydrated, and its water of hydration could react readily with POCl₃. However, an attempt using an excess of POCl₃ still gave a low yield of **17**. Preparation of Al(acphNC)₃ and Fe(acphNC)₃ (**14** and **15**), on the other hand, proceeded in 75% and 90% yield, respectively, relatively high values for the transformation of three identical functional groups in the same molecule.

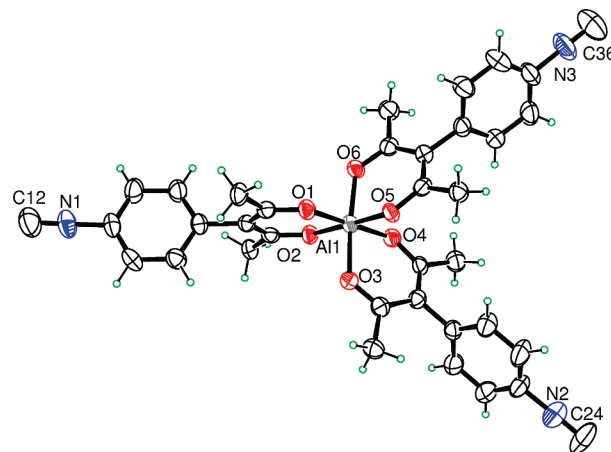


Figure 9. Ellipsoid plot of Al(acphNC)₃ (**14**), from the crystal structure of its hexane solvate.

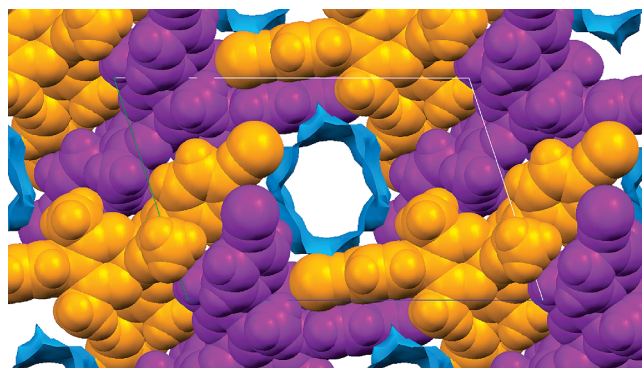


Figure 10. Illustration of the crystal structure of Al(acphNC)₃, viewed parallel to the *a* axis. One orientation of the Al(acphNC)₃ molecules is shown in purple, and the inversion-related orientation is in gold. The blue surfaces, calculated with a 0.9 Å probe radius and a 0.7 Å grid, enclose voids of ca. 400 Å³, or 21% of the unit cell volume.

The crystal structure of Al(acphNC)₃ (**14**) is shown in Figure 9. Molecules of Al(acphNC)₃ in the crystal are crudely trigonal in shape, but their CN···Al···NC angles (137.7°, 81.9°, and 140.3°) show large deviations from the ideal 120°. Similarly large distortions have been observed in the structures of Al(pyac)₃⁴³ and Fe(pyac)₃.^{7,9}

Initial solution of the crystal structure of Al(acphNC)₃ revealed molecules of **14**, but also a region with poorly defined electron density attributable to solvent molecules. Several approximately evenly spaced difference electron density peaks of similar intensity were observed in the solvent region, which suggested a hydrocarbon. Because hexane had been used in the crystallization process, our first model included disordered partially occupied hexane molecules in this region, with an overall formula of Al(acphNC)₃·0.5C₆H₁₄. For the final refinement, however, the solvent contribution to the data was removed using SQUEEZE⁴⁴ (in PLATON⁴⁵): approximately 58 electrons were removed per unit cell (corresponding to ca. 0.58 molecule of hexane per formula unit), and a void of

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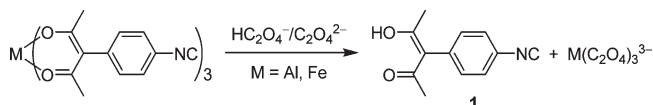


Figure 11. Displacement of metal ions from $\text{Al}(\text{acphNC})_3$ (**14**) and $\text{Fe}(\text{acphNC})_3$ (**15**) to produce the free isocyano- β -diketone ligand HacphNC (**1**).

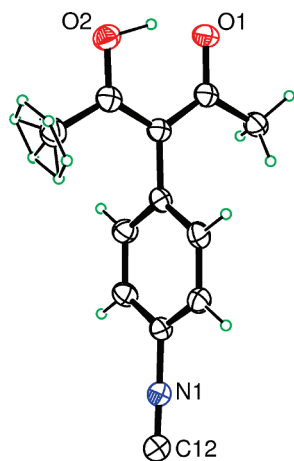


Figure 12. Crystal structure of HacphNC (**1**).

ca. $400 \text{ \AA}^3$ per unit cell was left behind, see Figure 10. This void has approximately the right volume for two hexane molecules (on the basis of the density of liquid hexane at 25°C , 0.655 g cm^{-3} , the volume of one molecule of hexane is approximately $219 \text{ \AA}^3$). Thus, it is possible that the crystals formed as $\text{Al}(\text{acphNC})_3 \cdot \text{C}_6\text{H}_{14}$ ($Z = 2$), but some hexane was lost during selection and mounting. This propensity for solvent loss is consistent with the microanalysis for **14** (see the Experimental Section), which fits well with the ansolvous compound.

Synthesis of HacphNC. We attempted to prepare the free HacphNC ligand (**1**) directly from **2** by treatment with POCl_3 . Spectra of this reaction mixture indicated that the formamide moieties were consumed (NMR) and isocyanide was formed (IR). However, the NMR spectra indicated that the β -diketone group was destroyed under the reaction conditions. Instead, we isolated HacphNC from its Al, Fe, and Zn complexes (**14**, **15**, and **17**).

We explored two strategies for obtaining HacphNC (**1**) from its complexes. First, we treated **14**, **15**, and **17** with dilute acetic acid; this produced the desired HacphNC , but only in low yields (ca. 10%). Second, we treated CH_2Cl_2 solutions of $\text{Al}(\text{acphNC})_3$ (**14**) and $\text{Fe}(\text{acphNC})_3$ (**15**) with aqueous solutions prepared from oxalic acid and oxalate salts as extractants. In this scheme (Figure 11), the H^+ from the acid is designed to protonate the coordinated β -diketonate ligand, and the oxalate is designed to complex the liberated Fe^{3+} . The procedure with $\text{Fe}(\text{III})$ has the advantage that the colors of $\text{Fe}(\text{acphNC})_3$ and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ make it easy to determine visually when the extraction of the metal ion into the aqueous layer is complete. With an excess of oxalate, we obtained HacphNC in 37% yield from $\text{Fe}(\text{acphNC})_3$; yields from $\text{Al}(\text{acphNC})_3$ were lower. The crystal structure of **1** (IR $\nu_{\text{C}\equiv\text{N}}$ 2122 cm^{-1}) is shown in Figure 12.

To explore the reactivity of the isocyanide moiety of HacphNC , we treated both the free ligand (**1**) and its Al

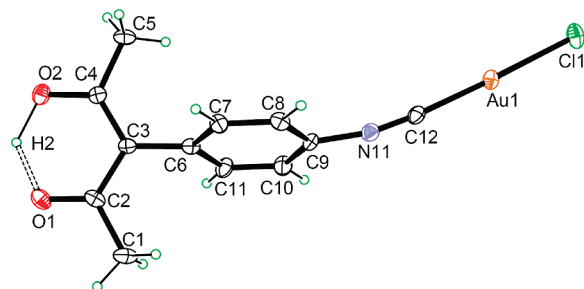


Figure 13. Crystal structure of HacphNCAuCl (**18**). Adjacent molecules in the crystal are arranged to form zigzag chains of weak $\text{Au} \cdots \text{Au}$ interactions ($3.466 \text{ \AA}$), similar to those previously reported for $(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})\text{AuX}$ ($\text{X} = \text{Br}, \text{I}$).³⁹

complex (**14**) with $(\text{Me}_2\text{S})\text{AuCl}$, giving HacphNCAuCl (**18**) and $\text{Al}(\text{acphNCAuCl})_3$ (**19**), respectively. These products were characterized by NMR and IR, and crystals of **18** suitable for X-ray analysis were also obtained (Figure 13). The $\nu_{\text{C}\equiv\text{N}}$ values are higher in the products compared to HacphNC (2122 cm^{-1}), as expected: 2223 and 2222 cm^{-1} for **18** and **19**, respectively. These values are very close to that observed by Uson et al. for PhNCAuCl (2230 cm^{-1}).⁴¹ The Al–Au complex **19** is an example in which both the soft (isocyanide) and hard (β -diketonate) moieties of HacphNC are coordinated to metal ions.

Conclusion

The first ligand combining isocyanide and β -diketone groups, 3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC), has been synthesized. The ligand was first prepared in the form of its Al, Fe(III), Cu(II), and Zn complexes. Treatment of the Al and Zn complexes with dilute acid, or of the Al and Fe complexes with $\text{C}_2\text{O}_4^{2-}/\text{HC}_2\text{O}_4^-$, liberates the target ligand HacphNC . The isocyanide moieties in both the free ligand HacphNC and its Al complex $\text{Al}(\text{acphNC})_3$ can also bind to Au(I). We are now extending the chemistry of HacphNC to metals that will yield higher coordination numbers, for the construction of 3D supramolecular structures.

Experimental Section

A Bruker DPX-250 instrument (250 MHz) was used for NMR spectroscopy. All IR spectra were performed on thin films with the use of a Bruker Tensor 27 spectrometer. Single-crystal X-ray diffraction data were collected with use of a Nonius KappaCCD instrument; the results are summarized in Tables 1 and 2. All experimental procedures were carried out in the air unless otherwise noted. Crystal-structure illustrations were prepared using CSD Mercury, version 2.2 (Figure 10) and Ortep-3 for Windows.

4-Formamidobenzaldehyde (OHC-4-C₆H₄NHCHO, 6). 4-Formamidobenzaldehyde was first synthesized by Hrvatin and Sykes³⁶ in formic acid/toluene. We obtained a higher yield of the product by using a mixture of ethyl formate and ethyl acetate as the reactant/solvent, and by adding the tin metal in two portions. 4-Nitrobenzaldehyde (6.04 g, 40 mmol) was dissolved in a mixture of formic acid (90%, 60 mL), ethyl formate (50 mL), and ethyl acetate (150 mL). The solution was refluxed under nitrogen with stirring. Tin metal (9.0 g, 76 mmol) was added in two equal portions: one immediately and the other after 24 h. The reaction was complete after three days, as judged by TLC. The solution was filtered hot and evaporated nearly to dryness. Toluene (300 mL) was added to the residue and the mixture refluxed with a Dean–Stark trap for about 2 h to remove the

Table 1. Crystal Data and Refinement Parameters for the Isocyano- β -diketone **1** and Related Compounds

compd	1	(<i>E</i>)- 2	(<i>Z</i>)- 2	(<i>E</i>)- 6	9
formula	C ₁₂ H ₁₁ NO ₂	C ₁₂ H ₁₃ NO ₃	C ₁₂ H ₁₃ NO ₃	C ₈ H ₇ NO ₂	C ₁₄ H ₂₀ NO ₈ P
fw	201.22	219.23	219.23	149.15	361.28
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>Pca</i> 2 ₁
<i>a</i> , Å	7.0820(15)	14.379(3)	13.289(2)	4.3910(15)	13.383(2)
<i>b</i> , Å	11.606(3)	10.339(2)	7.5180(15)	6.917(2)	17.884(2)
<i>c</i> , Å	12.427(3)	14.974(4)	11.561(2)	11.793(3)	13.509(3)
α	90	90	90	90	90
β	93.666(13)	91.296(15)	111.153(8)	97.81(2)	90
γ	90	90	90	90	90
<i>V</i> , Å ³	1019.3(4)	2225.5(9)	1077.2(3)	354.86(18)	3233.3(9)
<i>Z</i>	4	8	4	2	8
<i>T</i> , K	110	110	110	110	110
<i>D</i> _{calcd} , g cm ^{−3}	1.311	1.309	1.352	1.396	1.484
μ , mm ^{−1}	0.090	0.095	0.098	0.102	0.214
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	0.0539	0.0473	0.0424	0.0396	0.0233
<i>R</i> _w (all data)	0.1572	0.1194	0.1109	0.0995	0.0629

Table 2. Crystal Data and Refinement Parameters for Metal Complexes

compd	12 Cu(acphNH-CHO) ₂	13 ·2H ₂ O [<i>trans</i> -Zn(acphNHCHO) ₂ (H ₂ O) ₂]·2H ₂ O	14 ·0.58C ₆ H ₁₄ ^a Al(acphNC) ₃ ·0.58C ₆ H ₁₄	18 HacphNCAuCl
formula	C ₂₄ H ₂₄ CuN ₂ O ₆	C ₂₄ H ₂₈ N ₂ O ₈ Zn·2H ₂ O	C ₃₆ H ₃₀ AlN ₃ O ₆ ·0.58C ₆ H ₁₄	C ₁₂ H ₁₁ AuClNO ₂
fw	500.00	573.89	677.59	433.63
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	8.136(2)	12.442(5)	7.433(5)	14.638(3)
<i>b</i> , Å	7.480(2)	9.637(4)	13.510(10)	6.4219(12)
<i>c</i> , Å	17.771(4)	11.947(5)	20.66(2)	14.919(2)
α	90	90	107.65(3)	90
β	103.166(7)	114.60(2)	97.53(3)	117.761(6)
γ	90	90	94.57(3)	90
<i>V</i> , Å ³	1053.1(5)	1302.5(10)	1944(3)	1241.0(4)
<i>Z</i>	2	2	2	4
<i>T</i> , K	110	110	110	90
<i>D</i> _{calcd} , g cm ^{−3}	1.577	1.463	1.158	2.321
μ , mm ^{−1}	1.084	1.001	0.099	12.057
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	0.0543	0.0537	0.069	0.043
<i>R</i> _w (all data)	0.1385	0.1385	0.185	0.128

^a 0.58C₆H₁₄ was included in fw, *D*, and μ ; it represents the approximate amount of electron density removed by SQUEEZE⁴⁴ before final refinement. See text for details.

remaining water and formic acid. The mixture was filtered when it was still hot, and the filtrate was evaporated to dryness. The residue was chromatographed on silica gel with 2:1 ethyl acetate/hexane. Colorless crystals of the *E* conformer of **6** grew easily from the eluate by evaporation. Yield: 3.91 g (66%). MP: 134–136 °C (lit. 139 °C³⁶). ¹H NMR spectra of **6** show a mixture of *E* and *Z* conformers immediately on mixing. In CDCl₃, *E*: 7.24, 7.91 (E3–4, 4H, *AB*), 8.30 (E1, 1H, d), 8.91 (NH, 1H, d), 9.95 (E5, 1H, s). *Z*: 7.60 (Z1, 1H, s), 7.75, 7.88 (Z3–4, 4H, *AB*), 8.47 (NH, 1H, s), 9.94 (Z5, 1H, s). In DMSO-*d*₆, *E*: 7.40, 7.86 (E3–4, 4H, *AB*), 9.03 (NH, 1H, d), 9.89 (E5, 1H, s), 10.56 (E1, 1H, d). *Z*: 7.79, 7.89 (Z3–4, 4H, *AB*), 8.37 (NH, 1H, s), 9.89 (Z5, 1H, s), 10.64 (Z1, 1H, s).

3-(4-Formamidophenyl)pentane-2,4-dione (HacphNHCHO, 2). Compound **6** (2.56 g, 17.2 mmol) and phospholene **4** (2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene; 4.02 g, 19.2 mmol) were dissolved in 15 mL of dichloromethane under argon. The reaction was complete after 3 days, as judged by the disappearance of the aldehyde resonance in ¹H NMR. The solvent was removed, and the residue was chromatographed on silica gel with 2:1 ethyl acetate/hexane. Yield: 1.95 g (52%). MP (*Z*): 124 °C. Anal. Calcd for C₁₂H₁₃NO₃: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.59; H, 6.14; N, 6.48. Slow evaporation of solutions of **2** yields crystals. In most of our experiments, the crystals were of the *Z* conformer; in one case, we also obtained a small amount of the *E* conformer in crystalline form. However, solutions of either conformer quickly develop a second set of ¹H NMR resonances attributable to the other conformer.

In CDCl₃, *E*: 7.12, 7.18 (E3–4, 4H, *AB*), 8.19 (E1, 1H, d), 8.74 (E2, 1H, d). *Z*: 7.15, 7.58 (Z3–4, 4H, *AB*), 7.45 (Z1, 1H, s), 8.41 (Z2, 1H, s). Enol: 1.88 (CH₃, 6H, s), 16.66 (OH, 1H, s). Keto: 2.20 (CH₃, 6H, s), 4.83 (CH, 1H, s). In DMSO-*d*₆, *E*: 7.16, 7.23 (E3–4, 4H, *AB*), 8.84 (E2, 1H, d), 10.20 (E1, 1H, d). *Z*: 7.20, 7.62 (Z3–4, 4H, *AB*), 8.29 (Z2, 1H, s), 10.26 (Z1, 1H, s). Enol: 1.85 (CH₃, 6H, s), 16.79 (OH, 1H, s). Keto: 2.13 (CH₃, 6H, s), 5.30 (CH, 1H, s).

Al(acphNHCHO)₃ (10). A solution of Al(NO₃)₃·9H₂O (1.125 g, 3.00 mmol) in 15 mL of H₂O was added to a solution of HacphNHCHO (2.19 g, 10.0 mmol) in 15 mL of CH₃OH with stirring. Then, NaHCO₃ (0.756 g, 9.0 mmol) in 5 mL of H₂O was added. A light yellow precipitate formed, which was collected, triturated with H₂O (2 × 15 mL) and methanol (10 mL), and air-dried. Yield: 1.89 g (92%). Anal. Calcd for C₃₆H₃₆AlN₃O₉: C, 63.43; H, 5.32; N, 6.16. Found: C, 63.47; H, 5.33; N, 6.24. ¹H NMR (DMSO-*d*₆): 1.77 (s, Me, 18H). *E*: 7.18, 7.22 (E3–4, 12H, *AB*), 8.81 (E2, 3H, d), 10.18 (E1, 3H, d). *Z*: 7.14, 7.61 (Z3–4, 12H, *AB*), 8.28 (Z2, 3H, s), 10.23 (Z1, 3H, s).

Fe(acphNHCHO)₃ (11). A solution of Fe(NO₃)₃·9H₂O (3.43 g, 8.5 mmol) in 15 mL of H₂O was added to a solution of HacphNHCHO (6.65 g, 30.4 mmol) in 40 mL of CH₃OH with stirring. Then, NaHCO₃ (2.14 g, 25.5 mmol) in 25 mL of H₂O was added. A deep red precipitate formed, which was collected; washed with H₂O (2 × 15 mL), methanol (2 × 15 mL), and acetone (2 × 15 mL); and dried at 100 °C. Yield: 3.77 g (62%).

Cu(acphNHCHO)₂ (12). Cu(OAc)₂·H₂O (0.363 g, 1.82 mmol) in 7 mL of H₂O was added to a solution of HacphNHCHO

(0.92 g, 4.2 mmol) in 8 mL of methanol, with stirring. A blue-green precipitate formed, which was collected, washed with H₂O and methanol, and air-dried. Yield: 0.90 g (99%). Anal. Calcd for C₂₄H₂₄CuN₂O₆: C, 57.64; H, 4.84; N, 5.60. Found: C, 57.49; H, 4.63; N, 5.58. Crystals suitable for X-ray analysis were grown from DMSO/water.

trans-Zn(acphNHCHO)₂(H₂O)₂ (13). Solutions of Zn(OAc)₂·2H₂O (0.11 g, 0.50 mmol, in 5 mL of H₂O) and HacphNHCHO (0.22 g, 1.00 mmol, in 3 mL of CH₃OH) were mixed. NaHCO₃ (0.08 g, 1.0 mmol) in 2 mL of H₂O was added to this mixture, and a yellow precipitate formed immediately. The precipitate was collected; washed with dichloromethane, H₂O, and diethyl ether; and dried at 70 °C overnight. Yield: 0.11 g (40%). This material contained both *E* and *Z* conformers of its formamide moieties, as judged by its ¹H NMR spectrum immediately after dissolving in DMSO-*d*₆: 1.65 (s, Me, 12H). *E*: 7.16, 7.19 (E3–4, 8H, *AB*), 8.81 (E2, 2H, d), 10.13 (E1, 2H, d). *Z*: 7.14, 7.58 (Z3–4, 8H, *AB*), 8.28 (Z2, 2H, s), 10.18 (Z1, 2H, s). Meanwhile, light yellow single crystals of [trans-Zn(acphNHCHO)₂(H₂O)₂]₂·2H₂O (i.e., **13**·2H₂O, with *Z*-formamides) were obtained from the H₂O/methanol filtrate the next day; this material was suitable for X-ray analysis.

Al(acphNC)₃ (14). To a solution of Al(acphNHCHO)₃ (1.023 g, 1.50 mmol) and diisopropylamine (1.50 g, 14.8 mmol) in CH₂Cl₂ (50 mL) was added POCl₃ (0.690 g, 4.50 mmol) at room temperature under argon. After stirring for 1 h, the whole solution became clear. It was washed with 10% NaHCO₃ (20 mL), and the CH₂Cl₂ layer was separated and evaporated to 10–15 mL. Hexane was added to this solution to precipitate the powdery yellow product, which was dried at 70 °C. Yield: 0.710 g (75%). Anal. Calcd. for C₃₆H₃₀AlN₃O₆: C, 68.89; H, 4.82; N, 6.70. Found: C, 68.69; H, 4.81; N, 6.78. IR: 2121 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 1.87 (18H, s), 7.25, 7.41 (12H, *AB*). Single crystals of the hexane solvate of **14** suitable for X-ray diffraction were grown by vapor diffusion of hexane into a dichloromethane solution of the compound.

Fe(acphNC)₃ (15). To a mixture of Fe(acphNHCHO)₃ (2.65 g, 3.73 mmol) and diisopropylamine (5.56 g, 55.0 mmol) in CH₂Cl₂ (15 mL) was added POCl₃ (2.61 g, 17.0 mmol) at room temperature under argon and stirred for 2 h. The above solution was then washed with 10% NaHCO₃ (2 × 40 mL), and the CH₂Cl₂ layer was separated and evaporated to 5 mL. The addition of hexanes (100 mL) to this solution precipitated the powdery red product, which was collected, washed with 50 mL of hexanes, and dried at 70 °C. Yield: 2.20 g (90%). IR: 2126 cm⁻¹.

Cu(acphNC)₂ (16). To a mixture of Cu(acphNHCHO)₂ (**12**; 0.350 g, 0.70 mmol) and diisopropylamine (0.446 g, 4.4 mmol) in CH₂Cl₂ (20 mL) was added POCl₃ (0.220 g, 1.44 mmol) at room temperature under argon. The color slowly changed from blue to green. After stirring for 5 days, not all of the Cu(acphNHCHO)₂ had dissolved. The mixture was filtered and the filtrate washed with water (2 × 15 mL) and with 10% NaHCO₃(aq). When hexane was added to the dichloromethane phase, a brown gum separated. It could not be isolated in pure

form, even after trituration with several solvents, but its IR spectrum showed $\nu_{\text{C}\equiv\text{N}} = 2147 \text{ cm}^{-1}$.

Zn(acphNC)₂ (17). Zn(acphNHCHO)₂·2H₂O (0.163 g, 0.30 mmol) and ⁱPr₂NH (0.217 g, 2.15 mmol) were dissolved in dichloromethane (10 mL). POCl₃ (0.110 g, 0.72 mmol) was added slowly to the solution, with stirring. The whole solution became clear in 30 min. The solution was washed with 10 mL of 10% NaHCO₃(aq). The CH₂Cl₂ layer was separated, dried (Na₂SO₄), and evaporated to 10–15 mL, and hexane was added to precipitate the product as a yellow powder. Yield: 0.018 g (13%). IR: 2124 cm⁻¹. ¹H NMR (250 MHz, CDCl₃): 1.87 (12H, s), 7.23, 7.42 (8H, *AB*).

3-(4-Isocyanophenyl)pentane-2,4-dione (HacphNC, 1). The iron(III) isocyano- β -diketonate complex Fe(acphNC)₃ (**17**; 1.36 g, 2.07 mmol) was dissolved in 100 mL of dichloromethane. Oxalic acid (H₂C₂O₄·2H₂O, 2.52 g, 20.0 mmol) and potassium oxalate (K₂C₂O₄·H₂O, 33.12 g, 180.0 mmol) were dissolved in 200 mL of distilled water. These two solutions were stirred together for 20 min, and the red color in the organic layer disappeared, indicating that the reaction was complete. The organic phase was then separated, and the aqueous layer was extracted with 50 mL of dichloromethane. The organic phases were combined, dried over Na₂SO₄, and evaporated to ca. 3 mL. This residue was chromatographed with ethyl acetate–hexane (1:1 v/v). Yield: 0.46 g (37%). Anal. Calcd for C₁₂H₁₁NO₂: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.44; H, 5.36; N, 7.03. ¹H NMR (250 MHz, CDCl₃): 1.89 (6H, s), 7.23, 7.42 (4H, *AB*), 16.71 (1H, s). IR: 2122 cm⁻¹. Compound **1** decomposed at ca. 140 °C without melting. Crystals suitable for X-ray crystallography were grown by slow evaporation of a solution in ethyl acetate–hexane (1:2 v/v).

HacphNCAuCl (18). (Me₂S)AuCl (0.059 g, 0.20 mmol) and HacphNC (0.044 g, 0.22 mmol) were dissolved in CHCl₃ (3 mL) and refluxed for 1 h. The solution was evaporated at 45 °C to remove the solvent and Me₂S. The residue was dissolved in 0.6 mL of CHCl₃ and precipitated with 3 mL of hexanes. The precipitate was air-dried. Yield: 0.028 g (32%). ¹H NMR (250 MHz, CDCl₃): 1.88 (6H, s), 7.37, 7.60 (4H, *AB*), 16.75 (1H, s). IR: 2223 cm⁻¹. Crystals suitable for X-ray crystallography were grown from CHCl₃ by layering with hexanes.

Al(acphNCAuCl)₃ (19). Al(acphNC)₃ (**14**; 0.0314 g, 0.050 mmol) and (Me₂S)AuCl (0.0441 g, 0.150 mmol) were dissolved in 10 mL of CH₂Cl₂ and refluxed under nitrogen for 2 h. The solution was then evaporated to dryness. ¹H NMR (250 MHz, CDCl₃): 1.86 (18H, s), 7.34, 7.60 (12H, *AB*). IR: 2222 cm⁻¹.

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Supporting Information Available: X-ray data for compounds **1**, (*E*)- and (*Z*)-**2**, (*E*)-**6**, **9**, **12**, **13**·2H₂O, **14**·0.58C₆H₁₄, and **18**, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.