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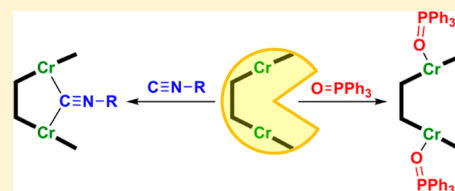
# Isocyanide and Phosphine Oxide Coordination in Binuclear Chromium Pacman Complexes

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**S** Supporting Information

**ABSTRACT:** The new binuclear chromium Pacman complex  $[\text{Cr}_2(\text{L})]$  of the Schiff base pyrrole macrocycle  $\text{H}_4\text{L}$  has been synthesized and structurally characterized. Addition of isocyanide,  $\text{C}\equiv\text{N-R}$  ( $\text{R} = \text{xylyl}$ ,  $t\text{Bu}$ ), or triphenylphosphine oxide donors to  $[\text{Cr}_2(\text{L})]$  gives contrasting chemistry with the formation of the new coordination compounds  $[\text{Cr}_2(\mu\text{-CNR})(\text{L})]$ , in which the isocyanides bridge the two Cr(II) centers, and  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$ , a Cr(II) phosphine oxide adduct with the ligands exogenous to the cleft.



The chemistry of binuclear, low-oxidation-state chromium complexes is dominated by a tendency to form metal–metal multiple bonds and an involvement in the activation of small molecules.<sup>1</sup> For example, quintuple M–M bond formation was demonstrated recently in binuclear Cr(I) complexes,<sup>2</sup> a new side-on bridging dinitrogen chromium complex was reported,<sup>3</sup> and dinitrogen reduction has been displayed at a Cr(0) center.<sup>4</sup> Industrially, chromium catalysts are used in the selective oligomerization and polymerization of olefins and there is ongoing interest in understanding and optimizing these processes.<sup>5</sup> Chromium complexes have been exploited as catalysts for other useful C–C bond forming reactions, including the coupling of alkyl halides with aldehydes and pinacol-type couplings.<sup>6</sup>

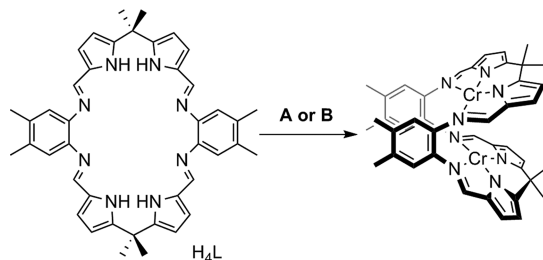
Strategies to define the formation and reactivity of binuclear complexes often involve the design of ligands that control both the primary coordination sphere of the metal and the separation between the metals. In this context, cofacial diporphyrins and their bimetallic complexes have displayed a diversity of small-molecule chemistry, but their exploitation is limited due to the complexity of the ligand synthesis.<sup>7</sup> In recent years a class of Schiff-base polypyrrole macrocycles ( $\text{H}_4\text{L}$ , Scheme 1) has been developed which fold upon metalation into structures reminiscent of cofacial or Pacman diporphyrins. A wide range of main-

group, late-transition-metal, lanthanide, and actinide complexes of these macrocycles have been synthesized,<sup>8</sup> of which cobalt complexes were found to be effective as catalysts for the reduction of dioxygen to water.<sup>9</sup> However, the early-transition-metal chemistry of either  $\text{H}_4\text{L}$  or cofacial diporphyrins remains a relatively unexplored field. We reported previously the syntheses of the Ti(III) and V(III) complexes  $[(\text{MCl})_2(\text{L})]$ , but could not structurally characterize either complex and did not carry out extensive investigation into their reactivity.<sup>10</sup> Herein, we report the synthesis and structure of the first binuclear chromium Pacman complex and its coordination chemistry with isocyanide and phosphine oxide donors.

The new binuclear chromium complex of the Pacman macrocycle  $[\text{Cr}_2(\text{L})]$  can be prepared either by addition of  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  to  $\text{H}_4\text{L}$  or by reaction of  $\text{K}_4\text{L}$  with  $\text{CrCl}_2$  (Scheme 1). Both reactions have comparable yields ( $\sim 70\%$ ), but salt elimination is preferred, since the synthesis of  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  is low yielding.<sup>11</sup> The  $^1\text{H}$  NMR spectrum of  $[\text{Cr}_2(\text{L})]$  in  $d_5$ -pyridine at 298 K shows paramagnetically broadened and contact-shifted resonances at 16.9, 14.0, 6.7,  $-29.2$ , and  $-97.7$  ppm, which are not assignable to specific ligand protons. Two broad, residual protio solvent resonances are visible in the room-temperature spectrum at 8.7 and 7.2 ppm. At 393 K, the resonance at 7.2 ppm separates into two sharper resonances at 7.3 and 7.2 ppm, indicating that pyridine binds transiently to the paramagnetic chromium complex in solution.

The X-ray crystal structure of  $[\text{Cr}_2(\text{L})]$  crystallized from benzene reveals that the macrocycle adopts a Pacman geometry (Figure 1). In the lattice, molecules of  $[\text{Cr}_2(\text{L})]$  are arranged in chains alternating with benzene molecules which engage in bonding to the *exo* faces of the macrocycles at a Cr–C contact distance of 3.608(2) Å. Both Cr(II) ions are bound in equivalent pseudo-square-planar environments comprising  $\text{N}_4$  pyrrolide and imine donor sets with the mean Cr–N(pyrrolide) distance

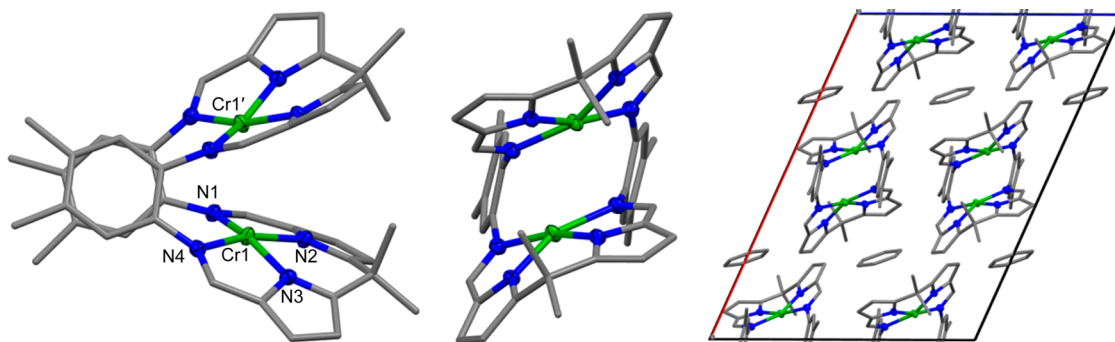
**Scheme 1. Synthesis of  $[\text{Cr}_2(\text{L})]$ <sup>a</sup>**



<sup>a</sup>Reagents: (A) 2  $[\text{Cr}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ , toluene; (B) (i) 4  $\text{KN}(\text{SiMe}_3)_2$ , (ii) 2  $\text{CrCl}_2$ , THF.

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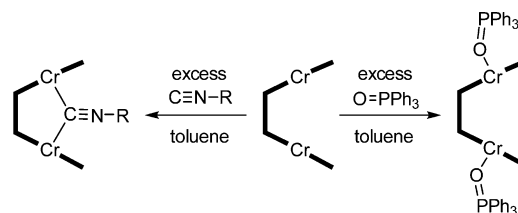
**Figure 1.** Solid-state structure of  $[\text{Cr}_2(\text{L})]$  illustrating the molecular geometry (left and center) and packing in the unit cell (right). For clarity, hydrogen atoms and lattice solvent are omitted (where shown, displacements ellipsoids are drawn at 50% probability). Selected bond lengths ( $\text{\AA}$ ) and angles (deg):  $\text{Cr1}\cdots\text{Cr1}' = 3.1221(1)$ ,  $\text{Cr1-N1} = 2.1139(16)$ ,  $\text{Cr1-N2} = 1.9702(15)$ ,  $\text{Cr1-N3} = 1.9758(15)$ ,  $\text{Cr1-N4} = 2.0780(15)$ ;  $\text{N1-Cr1-N2} = 80.06(6)$ ,  $\text{N2-Cr1-N3} = 85.52(6)$ ,  $\text{N3-Cr1-N4} = 78.64(6)$ ,  $\text{N4-Cr1-N1} = 114.02(6)$ .

of 1.97  $\text{\AA}$  shorter than the mean  $\text{Cr-N}(\text{imine})$  distance of 2.10  $\text{\AA}$ . The two pockets of the macrocycle are twisted with respect to each other in order to maximize favorable offset  $\pi$ - $\pi$  stacking interactions between the aryl hinges of the ligand. The sum of the four  $\text{N-Cr-N}$  angles is  $358^\circ$ , and the  $\text{Cr}(\text{II})$  ions are displaced 0.20  $\text{\AA}$  from the  $\text{N}_4$  plane into the macrocyclic cleft. The resulting  $\text{Cr}\cdots\text{Cr}$  separation of 3.1221(1)  $\text{\AA}$  is the shortest  $\text{M-M}$  distance observed in any  $[\text{M}_2(\text{L})]$  complex of this type.<sup>12</sup> In structures where two metal-metal-bonded  $\text{Cr}$  centers are supported by an  $\text{N}_4$  donor set,  $\text{Cr-Cr}$  bond lengths range from 1.86 to 3.00  $\text{\AA}$ , with a median value of 2.40  $\text{\AA}$ .<sup>13</sup> The  $\text{Cr-Cr}$  separation in  $[\text{Cr}_2(\text{L})]$  lies outside this range, and so it seems that there is no metal-metal bonding interaction. This is supported by the solution magnetic moment of  $[\text{Cr}_2(\text{L})]$  of  $6.34 \mu_{\text{B}}$  ( $\text{C}_6\text{D}_6/\text{THF}$ ), which approaches that for two independent (noncommunicating)  $\text{Cr}(\text{II})$  ions (spin only,  $6.93 \mu_{\text{B}}$ ). Full magnetic, EPR, and computational studies to elucidate the electronic structure of  $[\text{Cr}_2(\text{L})]$  and its adducts described below are ongoing.

The addition of Lewis base donors to Pacman complexes can result in the binding and activation of small-molecule substrates such as  $\text{O}_2$  and  $\text{N}_2$ .<sup>9b,14</sup> These donors bind to the metals in the *exo* coordination sites, thereby directing substrates to the *endo* intermetallic site and can also increase the electron density available at the metal centers. Isocyanide ligands  $\text{C}\equiv\text{NR}$  are isoelectronic with carbon monoxide but are better  $\sigma$  donors and generally poorer  $\pi$  acceptors.<sup>15</sup> Their electronic and steric properties are tunable by modification of the organic substituent  $\text{R}$ . Transition-metal isocyanide complexes have been shown to achieve  $\text{C-F}$  bond activation and selective hydrogenation of alkynes, nitriles, and isocyanides, as well as alkene polymerization.<sup>16</sup> Recently a coordinatively unsaturated  $\text{Co}(-\text{I})$  complex of bulky *m*-terphenyl isocyanides has been isolated and shown to bind dinitrogen, as well as undergoing reactions with a range of organic substrates.<sup>17</sup> In light of these advances, reactions between  $[\text{Cr}_2(\text{L})]$  and isocyanides were evaluated.

An excess of the isocyanides  $\text{C}\equiv\text{NR}$  ( $\text{R} = \text{Xyl}$ ,  ${}^t\text{Bu}$ ) was added to solutions of  $[\text{Cr}_2(\text{L})]$  (Scheme 2). Single crystals were obtained from the reaction carried out in fluorobenzene ( $\text{R} = \text{Xyl}$ ) and a  $\text{THF}/\text{C}_6\text{D}_6$  mixture ( $\text{R} = {}^t\text{Bu}$ ). Determination of the structures reveals the 1:1 *endo* adduct  $[\text{Cr}_2(\mu\text{-CNR})(\text{L})]$ , in which the isocyanide adopts a bridging position within the macrocyclic cleft instead of the anticipated 2:1 *exo* adduct (Figure 2). Although bimetallic complexes with bridging isocyanide ligands are common in late-transition-metal chemistry, those containing early transition metals are rare, with the only homobimetallic examples being two molybdenum and three

### Scheme 2. Reaction of $[\text{Cr}_2(\text{L})]$ with Isocyanides and Triphenylphosphine Oxide<sup>a</sup>

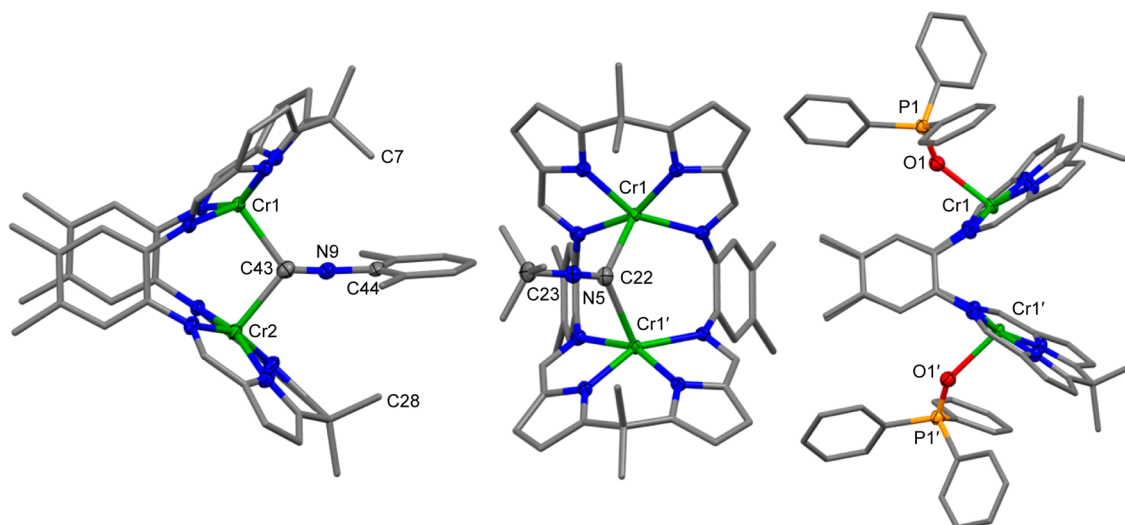


<sup>a</sup>The ligand architecture is shown in cartoon form.  $\text{R} = {}^t\text{Bu}$ , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$  (Xyl).

tungsten complexes.<sup>18</sup> To our knowledge  $[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$  and  $[\text{Cr}_2(\mu\text{-CN}{}^t\text{Bu})(\text{L})]$  are the first structurally characterized first-row early-transition-metal complexes featuring bridging isocyanide ligands.

The solid-state structures reveal that the isocyanides bridge the square-pyramidal  $\text{Cr}$  centers symmetrically. In  $[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$ , the planar xylyl ring is perpendicular to the aryl hinges of the macrocycle, minimizing steric interactions with the *endo*  $\text{Me}$  groups,  $\text{C7}$  and  $\text{C28}$ . One of the protons bound to  $\text{C7}$  is oriented toward the electron-rich  $\pi$  system of the isocyanide ligand ( $\text{C7}\cdots\text{C44} = 3.349(3)$   $\text{\AA}$ ,  $\text{C7}\cdots\text{N9} = 3.568(3)$   $\text{\AA}$ ) indicating that intramolecular hydrogen bonding occurs, similar to that seen in the related complex  $[\text{Cu}_2(\mu\text{-py})(\text{L})]$ .<sup>12</sup> In contrast, the three-dimensional steric bulk of the  ${}^t\text{Bu}$  group in  $[\text{Cr}_2(\mu\text{-CN}{}^t\text{Bu})(\text{L})]$  forces the isocyanide to protrude sideways out of the macrocycle jaws to avoid clashing with the *meso*  $\text{Me}$  groups (Figure 2, center). We reason that these steric constraints prevent the  ${}^t\text{Bu}$  isocyanide from approaching closer to the  $\text{Cr}$  centers, resulting in the longer  $\text{Cr-C}$  separation observed in  $[\text{Cr}_2(\mu\text{-CN}{}^t\text{Bu})(\text{L})]$  of 2.490(2)  $\text{\AA}$  in comparison to 2.259(2) and 2.261(2)  $\text{\AA}$  in  $[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$ .

Since these are the first binuclear chromium  $\mu\text{-CNR}$  complexes, comparison with later first-row transition-metal isocyanide complexes is instructive. A number of complexes containing the motifs  $\{\text{M}_2(\mu\text{-CNR})\}$  and  $\{\text{M}_3(\mu^3\text{-CNR})\}$  have been reported for both  $\text{CNXyl}$  and  $\text{CN}{}^t\text{Bu}$  for  $\text{M} = \text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$ . For the binuclear complexes, the mean  $\text{M-C}_{\text{CNR}}$  distance is 1.98  $\text{\AA}$ .<sup>13</sup> The longest  $\text{M-C}_{\text{CNR}}$  bond previously reported is 2.381(4)  $\text{\AA}$  in a binuclear  $\text{Fe}(\text{II})$  compound bridged by  $\text{CNMe}$ .<sup>19</sup> The long  $\text{Cr-C}$  distances observed in  $[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$  and  $[\text{Cr}_2(\mu\text{-CN}{}^t\text{Bu})(\text{L})]$  of 2.26 and 2.49  $\text{\AA}$ , respectively, are thus likely imposed by the ligand architecture.



**Figure 2.** Solid-state structures of  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  (left),  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$  (center), and  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$  (right). For clarity, hydrogen atoms and lattice solvent are omitted (where shown, displacement ellipsoids are drawn at 50% probability). The  $^t\text{Bu}$  group in  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$  was rotationally disordered, and the major conformer is shown. Selected bond lengths (Å) and angles (deg) are as follows  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$ :  $\text{Cr1}\cdots\text{Cr2} = 3.5877(5)$ ,  $\text{Cr1}-\text{C43} = 2.259(2)$ ,  $\text{Cr2}-\text{C43} = 2.261(2)$ ,  $\text{C43}-\text{N9} = 1.169(3)$ ;  $\text{Cr1}-\text{C43}-\text{Cr2} = 105.08(9)$ ,  $\text{C43}-\text{N9}-\text{C44} = 175.9(2)$ .  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$ :  $\text{Cr1}\cdots\text{Cr1}' = 3.7101(3)$ ,  $\text{Cr1}-\text{C22} = 2.490(2)$ ,  $\text{C22}-\text{N5} = 1.151(3)$ ;  $\text{Cr1}-\text{C22}-\text{Cr1}' = 96.35(7)$ ,  $\text{C22}-\text{N5}-\text{C23} = 172.8(2)$ .  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$ :  $\text{Cr1}\cdots\text{Cr1}' = 4.3120(5)$ ,  $\text{Cr1}-\text{O1} = 2.327(2)$ ,  $\text{O1}-\text{P1} = 1.497(2)$ ;  $\text{Cr1}-\text{O1}-\text{P1} = 137.6(1)$ .

In both  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  ( $\text{C43}-\text{N9}-\text{C44} = 175.9(2)^\circ$ ) and  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$  ( $\text{C22}-\text{N5}-\text{C23} = 172.8(2)^\circ$ ) the bridging isocyanide retains the linear geometry of the free ligand. This is not uncommon for a bridging isocyanide,<sup>20</sup> and the frequency of the  $\text{C}\equiv\text{N}$  stretching band in the IR spectrum is more indicative of the degree of back-donation to the isocyanide than its geometry. In the IR spectrum (Nujol mull) of  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$ ,  $\nu(\text{C}\equiv\text{N})$  is  $2150\text{ cm}^{-1}$ . This is shifted to slightly higher energy than in  $\text{CN}^t\text{Bu}$  ( $2132\text{ cm}^{-1}$ ) and indicates that a small amount of  $\pi$  back-donation occurs from the  $\text{Cr}(\text{II})$  centers to the isocyanide. The metal–ligand interaction is dominated by  $\sigma$  donation which occurs from a carbon-based orbital that is antibonding with respect to the  $(\text{C}\equiv\text{N})$   $\pi$  system of the isocyanide.<sup>21</sup> In contrast, two  $\text{C}\equiv\text{N}$  stretching bands are observed in the IR spectrum of  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  at  $1990$  and  $1970\text{ cm}^{-1}$ , a phenomenon which has been observed before in complexes containing a single bridging isocyanide and is attributed to solid-state effects.<sup>22</sup> These bands are shifted to considerably lower energy than in  $\text{CNXYl}$  ( $2114\text{ cm}^{-1}$ ), indicating that significant  $\pi$  back-donation occurs. This may be due to the greater  $\pi$ -acceptor ability of the conjugated aryl isocyanide in comparison to  $\text{CN}^t\text{Bu}$  and the shorter  $\text{Cr}-\text{C}_{\text{NIR}}$  separation in  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  in comparison to  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$ , allowing increased orbital overlap.

On a preparative scale  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  and  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$  may be synthesized in a number of different solvents in good yield. The reaction between  $[\text{Cr}_2(\text{L})]$  and  $\text{CNXYl}$  is instantaneous and is accompanied by a solution color change from dark red-brown to dark green.  $[\text{Cr}_2(\mu\text{-CNXYl})(\text{L})]$  is stable under dynamic vacuum and in THF solution. However, the  $^1\text{H}$  NMR spectrum recorded in  $d_5$ -pyridine shows resonances corresponding to  $[\text{Cr}_2(\text{L})]$  and a broad resonance at  $1.8\text{ ppm}$  attributed to the *o*-Me groups of the free isocyanide. This implies that coordination of pyridine to the Cr centers is competitive with isocyanide. In contrast,  $[\text{Cr}_2(\text{L})]$  reacts slowly with  $\text{CN}^t\text{Bu}$  at room temperature, though the reaction is complete within 48 h at  $80^\circ\text{C}$ . Once formed, the complex is stable under dynamic vacuum, in THF or pyridine solution, and even upon addition of

the highly Lewis basic 4-dimethylaminopyridine, which suggests that the sterically hindered isocyanide is kinetically trapped within the macrocyclic cleft. The magnetic moment of  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$  in  $\text{C}_6\text{D}_6$  solution is  $4.75\ \mu_{\text{B}}$ , significantly less than that of  $[\text{Cr}_2(\text{L})]$  ( $6.34\ \mu_{\text{B}}$ ), indicating that the presence of the isocyanide bridge increases the electronic communication between the two  $\text{Cr}(\text{II})$  centers.

The steric bulk of  $\text{CN}^t\text{Bu}$  is not sufficient to prevent it from coordinating within the macrocyclic cleft and thereby blocking the intermetallic reaction space. In light of this, an excess of triphenylphosphine oxide was added to a toluene solution of  $[\text{Cr}_2(\text{L})]$  (Scheme 2). This ligand is much bulkier than the isocyanides, and furthermore, phosphine oxides do not commonly adopt bridging modes in transition-metal complexes; only six examples have been structurally characterized.<sup>13</sup> Single crystals were isolated from the toluene solution, and X-ray analysis revealed the formation of the desired 2:1 *exo* adduct  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$ , in which one phosphine oxide coordinates to each  $\text{Cr}(\text{II})$  ion in the *exo* axial coordination site (Figure 2, right). The Cr centers adopt square-pyramidal geometries with a  $\text{Cr}-\text{O}$  distance of  $2.327(2)\text{ Å}$ . To our knowledge this is the first structurally characterized  $\text{Cr}(\text{II})$  phosphine oxide complex. A few phosphine oxide complexes of  $\text{Cr}(\text{III})$  have been reported, including a  $\text{Cr}(\text{III})$  porphyrin bearing chloride and triphenylphosphine oxide axial ligands.<sup>23</sup> These compounds feature markedly shorter  $\text{Cr}-\text{O}$  distances than in  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$ , ranging from  $1.83\text{ Å}$ <sup>24</sup> to  $2.03\text{ Å}$ ,<sup>23</sup> due to the increased electrostatic attraction between the O donor and the  $\text{Cr}(\text{III})$  cation.

$[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$  precipitates as a microcrystalline solid from toluene and may be redissolved in THF. However, the  $^1\text{H}$  NMR spectrum recorded in THF/ $\text{C}_6\text{D}_6$  shows resonances consistent with  $[\text{Cr}_2(\text{L})]$  and broad features in the aromatic region corresponding to the phenyl protons of free triphenylphosphine oxide. No resonances were present in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $298\text{ K}$ , but cooling to  $203\text{ K}$  resulted in a broad resonance at  $24\text{ ppm}$  corresponding to free  $\text{OPPh}_3$ . Therefore, in THF the phosphine oxide ligands are labile and an equilibrium is

likely established between the THF and phosphine oxide adducts of  $[\text{Cr}_2(\text{L})]$ .

Neither isocyanides nor phosphine oxides are suitable as *exo*-axial activating ligands for  $[\text{Cr}_2(\text{L})]$ . However, their reactions with the new chromium Pacman complex  $[\text{Cr}_2(\text{L})]$  illustrate the potential of this complex to bind substrates either *exo* to the cleft of the macrocycle or cooperatively between the two metals within the macrocyclic cleft. The flexibility of this class of Schiff base pyrrole macrocycle is also evidenced in this series of chromium complexes. Among the four complexes reported here the Cr...Cr separation varies by 1.19 Å and the bite angle of the jaws of the macrocycle by 19° (Table 1). The term “Pacman” was

**Table 1. Comparison of Selected Structural Data for the Different Chromium Pacman Complexes**

	Cr...Cr (Å)	bite angle (deg) <sup>12</sup>
$[\text{Cr}_2(\text{L})]$	3.1221(1)	48
$[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$	3.5877(5)	53
$[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$	3.7101(3)	56
$[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$	4.3120(5)	67

coined to describe the ability of bimetallic complexes to “chew” upon substrates of different sizes, and it is clearly an appropriate descriptor for  $[\text{Cr}_2(\text{L})]$ .<sup>25</sup> In ongoing work we are investigating the redox chemistry of the binuclear chromium Pacman complex and its solvates with a view to developing stoichiometric and catalytic transformations of small molecules.

**Experimental Section.** All reactions were carried out under an atmosphere of dry  $\text{N}_2$  using dry solvents and standard Schlenk and glovebox techniques. Isolated yields and elemental analyses of compounds are as follows.  $[\text{Cr}_2(\text{L})]$ : 72%. Anal. Calcd for  $\text{C}_{42}\text{H}_{40}\text{Cr}_2\text{N}_8$ : C, 66.30, H, 5.30, N, 14.73. Found: C, 66.10; H, 5.17; N, 14.68.  $[\text{Cr}_2(\mu\text{-CNXyl})(\text{L})]$ : 73%. Anal. Calcd for  $\text{C}_{51}\text{H}_{49}\text{Cr}_2\text{N}_9$ : C, 68.67; H, 5.54; N, 14.13. Found: C, 68.45; H, 5.42; N, 13.96.  $[\text{Cr}_2(\mu\text{-CN}^t\text{Bu})(\text{L})]$ : 83%. Anal. Calcd for  $\text{C}_{47}\text{H}_{49}\text{Cr}_2\text{N}_9$ : C, 66.89; H, 5.85; N, 14.94. Found: C, 66.78; H, 5.81; N, 14.86.  $[\text{Cr}_2(\text{OPPh}_3)_2(\text{L})]$ : 63%. Anal. Calcd for  $\text{C}_{78}\text{H}_{70}\text{Cr}_2\text{N}_8\text{P}_2\text{O}_2$ : C, 71.11; H, 5.36; N, 8.51. Found: C, 70.84; H, 5.45; N, 8.40.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Text, figures, tables, and CIF files giving full synthetic procedures,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR, IR and magnetic data (where appropriate), and details of single-crystal X-ray structure determinations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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