1s orbitals, is calculated to be lower in energy for the tetrahedron than for the square. Thus it is the energetic preferences of the occupied d block which control the geometry. The direct analogy with the orbitals of the H_5 cluster is lost.

The Stability of H_n Fragments

There has been some recent interest[41] in exploring the reasons underlying the stability of the symmetrical structures for cyclic conjugated hydrocarbons. For example, the D_{6h} structure of benzene, long the organic chemists prototypic "aromatic" molecule is predicted via a second-order Jahn–Teller effect to be unstable with respect to the structure with bond alternation. It is only the structural preferences of the σ framework which prevent the distortion occurring. (See ref 42 for a discussion of a similar balance in polyacetylene, polyacene, graphite, and related systems.) By way of contrast, for the isoelectronic molecules cyclic N_6 or H_6, theoretical results[41] suggest the opposite. In both cases the cyclic system is predicted to be unstable with respect to three separate N_2 or H_2 molecules, respectively. In H_6 there is of course no underlying framework of different symmetry to resist the deformation. The magnitude of the distortion away from such symmetric geometries has been identified in valence bond language[41] with the strength of the bond in the resulting diatomic. Clearly the strength of the linkage in H_2 and N_2 molecules is enormous and should favor the diatomic rather than the cyclic structure. This is also true of the polyhedral structures. Since we have focused on the structures of systems with a total of two skeletal bonding electrons, the bond order between each H–H contact will rapidly decrease as the cluster size increases. At some stage the strength of metal–hydrogen bonding will not be sufficient to stabilize the cluster relative to free or coordinated H_2 molecules. The balance between intrafragment forces of this type and the role of metal–hydrogen bonding requires orbital methods more exact than the ones we have used here. Whether stable complexes of transition-metal fragments with cyclic or polyhedral H_n molecules can be isolated needs to be seen. However, we do note that for triangular H_3 a soft distortion coordinate that involves the shortening of one H–H distance and the lengthening of the other two will lead to a facile transformation between the species $Cr(CO)_4(H_2)_2$ and $Cr(CO)_4(H_3)H$ which we have described elsewhere.[16] On the othe hand the HOMO–LUMO gap in H_3^+ is the largest possible for a two connected cyclic system (3β) which should encourage stability of the symmetric structure. There is no evidence for a soft stretching mode in Oka's experiments[43] on free H_3^+.

Thus in conclusion, the idea that polyhedral systems give rise to a good HOMO–LUMO gap if isoelectronic to their $H_n^{(n-2)+}$ analogues appears to be a good way to view the complexes of this paper. However, their stability relative to other isomers does not seem to be so readily predictable. In many cases slippage of an H_2 or H_3 unit can occur to involve other orbitals on the metal fragment.

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Appendix

The computations were of the extended Hückel type with the geometrical and electronic parameters as used in our previous study.[16] The distortions we investigated employed constnt metal–hydrogen (1.755 Å) and H–H (0.870 Å in H_3 and 1.00 Å for H_4 complexes) distances, but the metal–metal distances had to vary (from 3.36 to 2.50 Å in $Co_2(CO)_6(H_3)$, for example) in the motions which converted polyhedral species into those with bridging hydrides for example. Numerical results from calculations that involve the making and breaking of bonds are not at all reliable with use of our computational method, but association of stability with the presence of energy gaps for particular electron counts is probably quite good.

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(41) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089.
(42) Burdett, J. K. *Prog. Solid. State Chem.* **1984**, *15*, 173.
(43) Oka, T. *Phys. Rev. Lett.* **1980**, *45*, 531.

Synthesis of Bis(η^6-2,6-dimethylpyridine)metal (Ti, V, Mo) by Metal Vapor Deposition. Spectral Properties of Bis(η^6-2,6-dimethylpyridine)metal (Cr, Ti, V, Mo, Cr^+)

Edward J. Wucherer and Earl L. Muetterties†[1]

Department of Chemistry, University of California, Berkeley, California 94720

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The syntheses of bis(2,6-dimethylpyridine)metal sandwich compounds by metal atom–ligand cocondensation and solution-state redox reactions have been investigated. The new sandwich compounds bis(2,6-dimethylpyridine)metal (Ti, V, Mo, Cr^+) have been obtained. The IR, NMR/ESR, and UV–vis spectra of bis(2,6-dimethylpyridine)metal (Cr, Ti, V, Mo, Cr^+) are reported and used to compare π-bonding properties of η^6-benzene with those of η^6-(ortho-disubstituted)pyridine.

Introduction

In the course of investigating the interactions of transition metals with small unsaturated or aromatic organic molecules,[2] we noticed a lack of information about bis(heteroaromatic)metal sandwich compounds. While fer-

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† Deceased.

(1) Address correspondence to Prof. R. A. Andersen, UC—Berkeley.

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rocene, bis(benzene)chromium, and their carbocyclic congeners have long been the subject of theoretical, spectroscopic, and synthetic investigations,[3-13] only three binary heterocyclic complexes, bis(tetramethylthiophene)iron(II),[14] bis(arsabenzene)chromium,[15] and bis(2,6-dimethylpyridine)chromium (1),[16] are known. Since the carbocyclic sandwich compounds have provided an important basis for understanding metal–arene interactions, we hoped to gain an understanding of metal–heteroaromatic interations by studying the spectroscopic properties of bis(heteroaromatic)metal sandwich complexes.

The replacement of one CH unit in benzene for a nitrogen atom to form pyridine has several consequences. First, pyridine with its nitrogen lone pair can σ- and/or π-bond to transition metals. There are many examples of pyridine rings σ-bound to transition metals and a few examples of pyridine rings π-bound to transition metals.[17-19] While the introduction of methyl groups in the two and six ring positions should make σ-bond formation sterically less favorable, it is not a perfect solution since σ-bound complexes of 2,6-dimethylpyridine have been prepared.[20]

The electronegative nitrogen atom in the ring shifts and splits the benzene derived π-orbitals. Simple molecular orbital calculations place the HOMO and LUMO of pyridine about 3 eV lower in energy than those of benzene.[21] Consequently pyridine should be a poorer π-donor ligand and a better π-acceptor to a reference metal. Lastly, the electronegative nitrogen atom makes the α-H's of alkyl-substituted pyridines more acidic than their arene counterparts, raising the possibility of metal–C–H reactions. Such reactions have been noted for arene systems.[22]

Metal vapor synthesis is a valuable method for the production of bis(arene)metal compounds;[10] 1 was prepared by this method.[16] This paper describes the synthesis of the molecules $(\eta^6\text{-}2,6\text{-}Me_2C_5H_3N)_2M$ (M = Cr, Ti, V, Mo; 1–4) by metal vapor synthesis and $[(\eta^6\text{-}2,6\text{-}Me_2C_5H_3N)_2Cr][BF_4]$ (**5**) by oxidation of 1. The compounds were synthesized so that their chemical and physical properties could be compared with those of the related $(\eta^6\text{-}C_6H_6)_2M$ compounds. In the following paper the single-crystal X-ray crystallography of the substituted pyridine complexes **2**, **3**, and **5** is described.[23] Gas-phase ultraviolet photoelectron spectroscopy will be reported later.[24]

Experimental Section

All manipulations were carried out either in glass Schlenk ware on a vacuum line or in a glovebox. Tetrahydrofuran (THF), diethyl ether, toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone immediately before use. 2,6-Dimethylpyridine was degassed by repeated freeze–pump–thaw cycles and vacuum distilled from activated (15 h, 150 °C, 3×10^{-2} torr) 3-Å molecular sieves. Methylene chloride was distilled from sodium/lead (1:9) under nitrogen prior to use. Benzene-d_6 and toluene-d_8 were vacuum distilled from sodium/benzophenone directly onto samples. Bulk metals of 99.5% purity or higher (Alfa) were degassed prior to use. The $AgBF_4$ (Ozark) was used as supplied. Compound 2 reacted with predried alumina and filter-aid so these were not used in any stage of any reaction workup. Elemental analyses were performed by the UCB Microanalytical Laboratory. Mass spectra were obtained on either an AEI-MS12 or a Finnigan 4000 using electron-impact ionization at 10 eV. NMR spectra were obtained at 500.1 MHz for proton and 125.8 MHz for carbon on a Bruker AM-500 NMR spectrometer. Magnetic susceptibility measurements were carried out on a SHE Corp. 905 SQUID magnetometer. Electron paramagnetic resonance spectra were obtained on a Varian E-3 EPR spectrometer at 9.5 GHz (X-band). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 283 infrared spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8450A UV–vis spectrophotometer. Specifications and operating procedures for both the locally built, static, small-scale (3-L) metal vapor apparatus and the G. V. Planar VSP302A rotary large-scale (10-L) reactor are available in the literature.[19,25]

Cocondensations. Titanium, vanadium, chromium, manganese, niobium, molybdenum, ruthenium, and tungsten atom va-

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(2) Cf. (a) Johnson, A. L.; Muetterties, E. L.; Stoehr, J.; Sette, F. *J. Phys. Chem.* **1985**, *89*, 4071. (b) Wexler, R. M.; Muetterties, E. L. *J. Phys. Chem.* **1984**, *88*, 4037. (c) Wexler, R. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1984**, *106*, 4810. (d) Shanahan, K. L.; Muetterties, E. L. *J. Phys. Chem.* **1984**, *88*, 1996. (e) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283. (f) Kouba, J. K.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 1065. (g) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546. (h) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (i) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 2276.

(3) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47.

(4) Cloke, F. G. N.; Dix, A. N.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150.

(5) Cf. (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Elschenbroich, C.; Spangenberg, B.; Mellinghoff, H. *Chem. Ber.* **1984**, *117*, 3165. (c) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37. (d) Clack, D. W.; Warren, K. D. *Struct. Bonding (Berlin)* **1980**, *39*, 1. (e) Graves, V.; Lagowski, J. J. *J. Organomet. Chem.* **1976**, *120*, 397. (f) Klabunde, K. J.; Efner, H. F. *Inorg. Chem.* **1975**, *14*, 789. (g) Radonovich, L. J.; Zuerner, E. C.; Efner, H. F.; Klabunde, K. J. *Inorg. Chem.* **1976**, *15*, 2976. (h) Shustorovich, E. M.; Dyatkina, M. E. *Zh. Strukt. Khim.* **1961**, *2*, 49. (i) Boehm, M. C. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* **1982**, *37A*, 1193.

(6) (a) Maslowsky, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977. (b) Aleksanyan, V. T. *Vib. Spectra Struct.* **1982**, *11*, 107.

(7) Cyvin, S. J.; Brunvoll, J.; Schaefer, L. *J. Chem. Phys.* **1971**, *54*, 1517.

(8) Graves, V.; Lagowski, J. J. *Inorg. Chem.* **1976**, *15*, 577.

(9) (a) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45. (b) Weber, J.; Geoffroy, M.; Goursot, A.; Penigault, E. *J. Am. Chem. Soc.* **1978**, *100*, 3995.

(10) (a) Benfield, F. W. S.; Green, M. L. H.; Ogden, J. S.; Young, D. *J. Chem. Soc., Chem. Commun.* **1973**, 866. (b) Anthony, M. T.; Green, M. L. H.; Young, D. *J. Chem. Soc., Dalton Trans.* **1975**, 1419. (c) Cloke, F. G. N.; Green M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

(11) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

(12) Tairova, G. G.; Kvashina, E. F.; Krasochka, O. N.; Kichigina, G. A.; Shvetsov, Yu. A.; Lisetsky, E. M.; Atovmyan, L. O.; Borod'ko, Yu. G. *Nouv. J. Chim.* **1981**, *5*, 603.

(13) Elschenbroich, C.; Moeckel, R.; Zenneck, U.; Clack, D. W. *Ber. Bunsenges. Phy. Chem.* **1979**, *83*, 1008.

(14) Braitsch, D. M.; Kumarappan, R. *J. Organomet. Chem.* **1975**, *84*, C37.

(15) Elschenbroich, C.; Kroker, J.; Massa, W.; Wuensch, M.; Ashe, A. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 563.

(16) (a) Simons, L. H.; Riley, P. E.; Davis, R. E.; Lagowski, J. J. *J. Amer. Chem. Soc.* **1976**, *98*, 1044. (b) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1976**, *15*, 2735.

(17) (a) Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057. (b) Choi, H. W.; Sollberger, M. S. *J. Organomet. Chem.* **1983**, *243*, C39–41. (c) Morris, R. H.; Ressner, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 909.

(18) (a) Dimroth, K.; Thamm, R.; Kaletsch, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 207. (b) Schmidt, R. E.; Massa, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 213.

(19) Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273.

(20) Cf. (a) Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 229. (b) Busnot, A.; Busnot, F.; Leclaire, A.; Bernard, M. *Z. Anorg. Allg. Chem.* **1983**, *503*, 207.

(21) Jorgensen, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic: New York, 1973.

(22) (a) Bandy, J. A.; Green, M. L. H.; O'Hare, D.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1402. (b) Bandy, J. A.; Cloke, F. G. N.; Green, M. L. H.; O'Hare, D; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 240. (c) Baretta, A.; Chong, K. S.; Cloke F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861.

(23) Wucherer, E. J.; Muetterties, E. L. *Organometallics*, following paper in this issue.

(24) Work in progress Dr. J. C. Green.

(25) (a) Shriver, D. F., Ed, *Inorganic Syntheses XIX*; Wiley-Intersciences: New York, 1979. (b) Moskovits, M.; Ozin, G. A., Eds. *Cryochemistry*; Wiley-Interscience: New York, 1976. (c) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. (d) Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Verlag: Heidelberg, 1979. (e) Wucherer, E. J. Ph.D. Thesis, UC—Berkeley, 1985.

pors were cocondensed with 2,6-dimethylpyridine. All reactions were worked up as described for 1 below. The extraction procedure led to the isolation of sandwich compounds in the case of titanium, vanadium, chromium, and molybdenum. The product from the manganese reaction was not soluble in THF or hydrocarbon solvents. All other reactions, whether sandwich compounds were isolated or not, yielded black-brown solid materials. These solids were obtained at each stage of the extraction procedure and could not be crystallized or purified. Elemental analysis showed an approximate metal to ring ratio of 1:1. An oily yellow product could be obtained from aqueous HCl workup of the materials. Mass spectra indicated that the oil was dimerized ligand and NMR showed that a number of isomers were present. Since alkyl pyridines are known to react with Raney nickel to produce a variety of isomeric dimers,[26] this product was not further investigated.

Cocondensations experiments using chromium atoms and either pyridine or 2,5-dimethylfuran did not show any sign of reaction. Reaction of chromium atoms with pyrrole, 1-methylpyrrole, 2,5-dimethylpyrrole, and 1,2,5-trimethylpyrrole resulted in small amounts of red oil which was not further investigated. When thiophene or 2,5-dimethylthiophene was reacted with chromium atoms, the metallic residue contained 5% sulfur but only traces of carbon and hydrogen. Similar observations have been reported by others.[16]

(η^6-2,6-$C_7H_9N)_2$Cr (1). Chromium metal (1.07 g, 20.6 mmol) and 2,6-dimethylpyridine (66.7 g, 622 mmol) were cocondensed over 2 h onto the liquid-nitrogen-cooled walls of a stationary 3-L (small scale) reaction flask. The Cr was sublimed from a 0.005-in. thick tungsten boat using 360–420 W. After cocondensation was complete, the matrix was allowed to melt under an argon atmosphere to a red-brown solution. Excess dimethylpyridine was removed under reduced pressure, and the resulting solid residue was extracted with 100 mL of THF. The deep red-brown THF solution was filtered through a Whatman GF/F glass microfiber filter, and the filtrate was evaporated to dryness under reduced pressure. The resulting brown solid was extracted with diethyl ether and filtered similarly. The filtrate was again evaporated to dryness. The dried, brown, ether-soluble extract was treated with 100 mL of pentane and filtered, the solvent was removed, and the resulting brown solid was sublimed (5×10^{-2} torr, 50–60 °C). The sublimate was dissolved in 5 mL of warm (40 °C) hexane and slowly cooled to 4 °C and then, over a period of 3 days, to −70 °C. The hexane was decanted cold, leaving 1 (0.36 g, 1.3 mmol, 6.5% based on the amount of chromium evaporated) as shown by comparison with the reported ^{1}H NMR spectrum.[16]

(η^6-2,6-$C_7H_9N)_2$Ti (2). Titanium metal (2.26 g, 47.2 mmol) was evaporated at 390 W, over 6 h, from electron bombardment furnaces in a large scale, rotary, metal-vapor synthesis plant. It was later determined that 1.01 g (21.1 mmol) of metal had actually reached the reaction surface. 2,6-Dimethylpyridine (263 g, 2.45 mol) was cocondensed with the metal. When cocondensation was complete, the matrix was allowed to melt and was worked up as described for compound 1 above. A deep burgundy-red microcrystalline solid was obtained (61 mg, 1%). MS; M$^+$ (1.9%) 262, M$^+$ − H$_2$ (1.4%) 260, $C_7H_9N^+$ (100%) 107. Anal. Calcd for $C_{14}H_{18}N_2Ti$: C, 64.1; H, 6.92; N, 10.7; Ti, 18.3. Found: N, 11.0; Ti, 17.5.

(η^6-2,6-$C_7H_9N)_2$V (3). The compound was prepared as for 2 above from vanadium metal (2.45 g evaporated, 0.843 g on reactor surface, 16.5 mmol) and 2,6-dimethylpyridine (145 g, 1.35 mol) over $3^3/_4$ h at 410-W electron bombardment power. Large dark red-brown crystals were isolated (1.71 g, 6.45 mmol, 39%). MS; M$^+$ (55%) 265, M$^+$ − H$_2$ (44%) 263, $C_7H_9N^+$ (100%) 107. Anal. Calcd for $C_{14}H_{18}N_2V$: C, 63.4; H, 6.84; N, 10.6; V, 19.2. Found: C, 63.0; H, 6.86; N, 10.4; V, 18.6.

(η^6-2,6-$C_7H_9N)_2$Mo (4). This compound was prepared as for 2 above from molybdenum (4.19 g evaporated, 1.53 g on reactor surface, 15.9 mmol) and 2,6-dimethylpyridine (205 g, 1.91 mol) over 5 h at 800–1200-W electron bombardment power. Needle-shaped, red-orange crystals were isolated (405 mg, 1.31 mmol, 8%). MS; M$^+$ (12%) 312, M$^+$ − H$_2$ (9%) 310, $C_7H_9N^+$ (100%) 107. Anal. Calcd for $C_{14}H_{18}MoN_2$: C, 54.3; H, 5.85; Mo, 30.9; N, 9.03. Found: C, 54.4; H, 6.01; Mo, 29.4; N, 9.0.

(η^6-2,6-$C_7H_9N)_2$CrBF$_4$ (5). Silver tetrafluoroborate (0.10 g, 0.514 mmol) and 1 (0.145 g, 0.544 mmol) were stirred in 25 mL of diethyl ether for 3 h, after which time the ether was removed under reduced pressure. The resulting black solid was washed with 30 mL of hexane and then extracted with 35 mL of methylene chloride. A yellow solution was obtained after filtration (Whatman GF/F). The solution was reduced in volume to 10 mL by vacuum distillation. Hexane (50 mL) was then carefully layered on top of the methylene chloride solution, and the system was slowly cooled (2 days) and kept (5 days) at −70 °C. Orange needle- and plate-shaped crystals were obtained (0.140 g, 0.396 mmol, 77%). Anal. Calcd for $C_{14}H_{18}BCrF_4N_2$: C, 47.6; H, 5.14; N, 7.93. Found: C, 47.2; H, 5.04; N, 7.85.

Results and Discussion

Reactions of titanium, vanadium, chromium, manganese, niobium, molybdenum, ruthenium, and tungsten atom vapors with 2,6-dimethylpyridine have been carried out. Bis(2,6-dimethylpyridine)metal (Cr, Ti, V, Mo) (1–4) could be reproducibly isolated in 6, 1, 39, and 8% yields, respectively. The compounds are air-sensitive, soluble in aliphatic hydrocarbons, and easily volatile.

Without matrix-isolation studies we can only speculate about the nature of the metal–dimethylpyridine interactions in the cocondensation reactions. It has not been possible to vary the reaction conditions; in each case the cocondensations were carried out with the maximum excess of ligand at the lowest temperature possible. The influence of such factors as the matrix temperature, the electronic state(s) of the metal atoms, the formation and lability of metal aggregates, and the intense light emitted by the hot metal targets is unknown.

Attempted oxidation and reduction reactions of the compounds 1–4 using sodium/benzophenone, or cobaltocene for reductions or ferrocenium, silver(I), or tropylium for oxidations, were only successful for the oxidation of 1 to the monocationic compound bis(2,6-dimethylpyridine)chromium tetrafluoroborate (5). This salt is stable for weeks in dry air, but acetone (1 day) or methylene chloride (2 weeks) solutions decompose slowly under argon.

The infrared spectra of compounds 1–5 are listed in Tables I and II. Assignments were made by comparison of the sample spectra with the spectrum of the pure ligand and by comparison with the assigned bis(benzene)metal spectra.[6,7,27] A number of bands or, more correctly, band patterns can be readily identified in both ligand and complex spectra. The "Kekule" ring deformation at 1225 cm^{-1}, the pattern of four bands in the region 1095–970 cm^{-1}, and the sharp single absorption at 540 cm^{-1} in the ligand spectrum are seen in each of the spectra for the complexes. While the in-plane aromatic C–H stretch at 3070 cm^{-1} is not significantly shifted upon coordination, the two sets of ligand in-plane aromatic C–C vibrations around 1585 and 1450 cm^{-1} appear to be shifted to lower energy by about 80 cm^{-1} and are drastically reduced in intensity. A similar shift has been reported for aromatic C–C stretches in bis(arene)metal compounds,[6,7] but unshifted bands could also be identified. Surprisingly, although it is also a C–C stretching motion, the "Kekule" distortion at 1225 cm^{-1} does not show a significant shift upon coordination.

The lowest frequency γ-CH of benzene (673 cm^{-1}) shifts to 794 cm^{-1} upon π-complexation with chromium; this is a result of kinematic coupling of the CH motion with the

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(26) Badger, G. M.; Sasse, W. H. F. *Adv. Heterocyclic Chem.* **1963**, *2*, 179. See also comments in ref 18a.

(27) (a) Green, J. H. S. *Spectrochim. Acta, Part A* **1970**, *26A*, 1523. (b) Green, J. H. S.; Harrison, D. J.; Kynaston, W.; Paisley, H. M. *Spectrochim. Acta, Part A* **1970**, *26A*, 2139. (c) Verdonck, L.; Van der Kelen, G. P.; Eeckhaut, Z. *Spectrochim. Acta, Part A* **1973**, *29A*, 813. (d) Draeger, J. A. *Spectrochim. Acta, Part A* **1983**, *39A*, 809.

Table I. Ligand-Based Vibrational Spectra of $(C_7H_9N)_2M$[a]

Cr (1)	Ti (2)	V (3)	Mo (4)	Cr^+ (5)	C_7H_9N	assign[b]
3050 m	3050 s	3050 m	3040 vs	3100 m	3070	ν_{CH}
					1595	ν_{CC}
1510 br w	1520 br w	1505 w	1505 s	1515 m	1580	ν_{CC}
					1470	ν_{CC}
			1365 s	1385 vw	1411	ν_{CC}
				1305 br w		
1320 w	1285 br vs	1290 br vs	1335 m	1290 br w	1265	ν_{CC}
1210 w	1200 m	1205 w	1210 w	1220 w	1225	kekule
1120 w		1100 br w		BF_4[c]	1155	β_{CH}
1057 w	1035 br s	1045 m	1055 s	BF_4[c]	1095	β_{CH}
1025 w	1025 br vs	1025 vs	1020 br s	BF_4[c]	1030	CH_3 rock
985 w	975 s	975 m	980 m	BF_4[c]	995	breathing
945 w	920 s	933 s	945 br w	BF_4[c]	970	CH_3 rock
840 br vw		880 vw		845 w	970	γ_{CH}
860 br vw		850 m	825 w	825 vw	905	γ_{CH}
805 br w	765 vs	755 s	715*/s	795 br w	770	γ_{CH}
740 br vw				770 vw		
720 br m	705 vs	710 m	715*/s	710 w	730	ϕ_{CC}
			700 m		716	α_{CCC}
645 w	625 m	640 w	640 w	665 m		
		580 w		550 br m	560	α_{CCC}
560 w	530 w	540 m		525 vs	540	α_{CCC}
405 w	400*/m	418*/vs	430*/br s	420 s	430	β_{CCH_3}
				405 w	417	ϕ_{CCC}

[a] In cm^{-1}; α = in-plane skeletal deformation, β = in-plane CH deformation, γ = out-of-plane CH wag, ϕ = out-of-plane skeletal deformation, ν = stretch, * = more than one mode assigned to this absorption. [b] References 6, 7, and 27. [c] Absorption due to BF_4^-.

Table II. Skeletal Deformations of Bis(aromatic)metal Compounds[a]

complex	assym	assym tilt	sym tilt	ref
$(C_7H_9N)_2Cr$ (1)	500 vw	480 vs	350 w	*b*
$(C_6H_6)_2Cr$	490	459	335	*c*
$(C_7H_9N)_2Ti$ (2)		410 vs 400* m		*b*
$(C_6H_6)_2Ti$	452	411	307	*c, d*
$(C_7H_9N)_2V$ (3)	490 w	450 vs 418 vs	330 w	*b*
$(C_6H_6)_2V$	478	439		*c*
$(C_7H_9N)_2Mo$ (4)	430* br s	390 s 375 vs		*b*
$(C_6H_6)_2Mo$	424	362		*c*
$(C_7H_9N)_2Cr^+$ (5)		475 vs 460 s	345 m	*b*
$(C_6H_6)_2Cr^+$	466	415		*c*

[a] In cm^{-1}; * = more than one mode assigned to this absorption; assym = ring–metal–ring assymmetric stretch; assym tilt = ring–metal–ring assymmetric tilt. [b] This work. [c] References 6 and 7. [d] Reference 12.

Table III. Magnetic Parameters for Vanadium and Chromium(1+) Sandwich Compounds

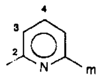
complex	*g*	*A*	$\bar{\mu}_{eff}$	ref
$(C_7H_9N)_2V$ (3)	1.977	56.9	1.75	*a*
$(C_6H_6)_2V$	1.987	62.7	1.73	*b, c*
$(C_7H_9N)_2Cr^+$ (5)	1.975	14.2	1.82	*a*
$(C_6H_6)_2Cr^+$	1.987	18.0	1.77	*c, d*
$(m\text{-}C_8H_{10})_2Cr^+$	1.987	17.6		*c, d*

[a] This work. [b] Reference 4. [c] Reference 3. [d] Reference 13.

Table IV. NMR Parameters for $(C_7H_9N)_2M$ (M = Cr (1), Ti (2), Mo (4))[a]

positn	1	2	4	ligand
		A. ^1H NMR		
m	2.330 s	2.213 s	2.172 s	2.4 s
3	4.382 d (5.3)	4.977 d (7.0)	4.806 d (4.9)	6.55 d
4	4.299 t (5.3)	4.286 t (7.0)	4.704 t (4.9)	6.99 t
		B. ^{13}C NMR		
m	22.66 q (127)	23.95 q (128)	23.49 q (128)	24.4
2	108.06 m	119.64 m	108.60 m	157.5
3	78.65 dm (169)	90.50 dm (169)	81.63 dm (169)	120.0
4	77.62 dt (172, 2)	73.03 dt (175, 2)	78.08 dt (173, 3)	136.3

[a] In benzene-d_6 at 17 °C. Chemical shifts in ppm and *J* values in parentheses in Hz.



metal atom.[7] Similar shifts have been observed for benzene and pyridine absorbed on transition-metal, single-crystal surfaces.[28] The shift for complexes **1–5** is considerably less or even in the opposite direction, i.e., from 770 to 805–755 cm^1. Another unusual feature arises from the three bands in the ligand spectrum at 716, 560, and 540 cm^{-1}. Upon complexation the ligand low-energy band at 540 cm^{-1} appears between 560 and 525 cm^{-1} with the same shape and relative intensity. The middle and upper bands originally at 560 and 717 cm^{-1} are difficult to identify in the spectra of **1–5**. The sandwich complexes have absorptions in the range 665–625 cm^{-1}, an area in which the ligand itself does not have any absorptions. We propose that the ligand 717 cm^{-1} band is lowered by ca. 80 cm^{-1} upon complexation and that the 560 cm^{-1} band loses intensity or combines with the 540 cm^{-1} absorption.

The vibrational modes of the ring–metal skeleton (500 to 300 cm^{-1}) are presented in Table II. Since the complexes **1–5** can have maximal C_{2v} symmetry, the degenerate symmetric (E_{1g}) and asymmetric (E_{1u}) ring-tilting vibrations of bis(benzene)metal complexes must each split into two bands. This is readily seen for the asymmetric tilt of compounds **1–5**. The absorptions for the bis(2,6-dimethylpyridine)metal complexes are generally at slightly higher energy than their benzene analogues even though the pyridine ligand has a higher mass. This is possibly an indication of stronger metal–ring bonding.

The infrared spectra confirm the sandwich structures of compounds **1–4** in solution (they dissolve in Nujol). As is the case for benzene, the π-bonding of the rings to the

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[28] (a) DiNardo, N. J.; Avouris, Ph.; Demuth, J. E. *J. Chem. Phys.* **1984**, *81*, 2169. (b) Coudana, R.; Gilles, J.-M.; Lucas, A. A.; Eds, *Vibrations at Surfaces*; Plenum: New York, 1982.

Table V. Absorption Maxima from UV-Vis Spectra of Sandwich Compounds[a]

compound	charge transfer ($\epsilon \times 10^{-3}$)	d–d (ϵ)	ref
$(C_7H_9N)_2Cr$ (1)	331 (9)	426 (300)	*b*
$(C_6H_6)_2Cr$	320 (8)	641 (25)	*c*
$(C_7H_9N)_2Ti$ (2)	367 (10)	494 (20)	*b*
$(C_6H_6)_2Ti$	355 (20)	501 (500)	*d*
$(C_7H_9N)_2V$ (3)	338 (8)	468 (800)	*b*
$(C_7H_9N)_2Mo$ (4)	330 (7)	428 (200)	*b*
$(C_7H_9N)_2Cr^+$ (5)	233 (13)		*b*
	274 (12)		
	280 (11)		
	290 (9)		
	349 (8)		
$(C_6H_6)_2Cr^+$	234 (14)	395 (560)	*c*
	270 (6)	1170 (7)	
	340 (6)		

[a] In nm; 1–4 in hexane, 5 in CH_2Cl_2. [b] This work. [c] References 9 and 11. [d] Reference 12.

metal atom is accompanied by a reduction of the ring C–C vibrational frequency, a result of reduced ring C–C bond order. This could be due to either the donor or acceptor character of the ring–metal–ring bonding.

The magnetic parameters for compounds **1**–**5** are similar to their benzene counterparts as shown in Tables III and IV. Variable-temperature, variable field magnetic susceptibility measurements indicate that compounds **3** and **5** follow Curie–Weiss behavior from 5 to 300 K with effective moments of 1.75 and 1.82 μ_B respectively, with Θ in each case being –3 K. In light of the spectroscopic and calculational work of Cloke et al.,[4] it is interesting to note that the hyperfine coupling constants *A* for **3** and **5** are slightly less than their bis(benzene) analogues; this could arise from improved metal–ligand overlap.

A variety of bis(substituted benzene)metal sandwich complexes have been studied by ^{13}C NMR spectroscopy.[8] It was found that π-coordination of a chromium atom to monosubstituted benzene rings quenched the effects of the substituent on the meta and para ^{13}C chemical shifts. A similar effect can be seen for the meta and para carbon atoms in **1** and **4** such that their ^{13}C shifts approach the bis(benzene)chromium value of 74.6 ppm. The titanium compound **2** does not follow this pattern. It has been pointed out that the loss of cylindrical symmetry upon changing pyridine for benzene should result in a higher barrier to ring rotation.[29] While the ring spinning could not be stopped in **1**[16] (–68 °C), we thought perhaps **2**, seemingly the least symmetrically sandwiched species, might display hindered ring rotation. This was not the case, as only slight broadening of the NMR signals was observed to –90 °C.

Electronic spectra of bis(benzene)sandwich compounds have not been extensively investigated.[9,11,12] Table V presents our results and the information reported for the benzene complexes. The properties of **1**–**5** agree in general with the results obtained for the benzene complexes, especially in the charge-transfer (short wavelength) region. The d–d transition energies of the benzene and pyridine chromium species are, however, rather different. Bis(2,6-dimethylpyridine)chromium (**1**) has an absorption at 426 nm while bis(benzene)chromium absorbs at 641 nm, a difference of 215 nm (0.98 eV). A stabilization of the HOMO of 1.45 eV has been calculated when benzene is replaced by pyridine[30] in bis(benzene)chromium; therefore such a shift in the electronic spectrum is a reasonable consequence of the expected reordering of the orbital energies. While data for bis(benzene)molybdenum are not available for comparison, the compound is described as green.[10] The pyridine complex **4** is red-orange like the chromium complex **1**. We therefore also expect different d–d transitions for the benzene and pyridine molybdenum complexes. Conversely, the spectra of the benzene and pyridine titanium complexes are nearly identical. Either the various effects of pyridine vs. benzene coordination cancel or the nature of the π-bound ring simply has little effect on the electronic states of the titanium sandwich complexes.

Summary

Bis(η^6-2,6-dimethylpyridine)metal complexes (Cr, Ti, V, Mo; **1**–**4**) have been synthesized by metal atom–ligand cocondensation reactions. $[(\eta^6\text{-}2,6\text{-}Me_2C_5H_3N)_2Cr][BF_4]$ (**5**) has been produced by solution-state oxidation of **1**. Attempted syntheses of bis(η^6-2,6-dimethylpyridine)metal complexes of other metals and oxidation states were unsuccessful, probably a result of nitrogen lone pair–metal σ or C–H–metal reaction pathways. The spectral properties of the bis(2,6-dimethylpyridine)metal sandwich complexes indicate that they are structurally and electronically quite similar to the bis(benzene)metal sandwich complexes. The largest differences appear in the electronic spectra of the bis(benzene)chromium and bis(dimethylpyridine)chromium species.

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Registry No. **1**, 59420-07-4; **2**, 108534-90-3; **3**, 108534-91-4; **4**, 108534-92-5; **5**, 108534-94-7; Cr, 7440-47-3; Ti, 7440-32-6; V, 7440-62-2; Mo, 7439-98-7; 2,6-C_7H_9N, 108-48-5.

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[29] Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

[30] Clack, D. W.; Warren, K. D. *Inorg. Chimica Acta* **1979**, *33*, 35.