of the pH range, either the $-NH_3^+$ group is deprotonated or the $-CO_2^-$ group is protonated, the interactions are diminished, and rearrangement may be possible to a smaller, more soluble form. In materials such as Myocrisin, adjacent substituents bear negative charges ($-CO_2^-$), giving repulsive interactions; in these cases, smaller cyclic units are likely, consistent with their ready solubility.

The $^{197}$Au Mössbauer spectrum of Auranofin is consistent with the linear S–Au–P stereochemistry recently established by X-ray crystallography.[17]

**Acknowledgment.** We are grateful to SRC for the award of a Research Studentship to K.B., Dr. M. Friedman, Johnson Matthey Research Laboratories, May and Baker Ltd., Sigma London Chemical Co., and Smith Kline and French Laboratories for generous gifts or loans of chemicals, and Professor C. E. Johnson for the loan of a $^{196}$Pt Mössbauer source.

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(17) Hill, D. T.; Sutton, B. M. *Cryst. Struct. Commun.* **1980**, *9*, 679.

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# Bis(2,2′-bipyridyl)diisopropoxymolybdenum(II). Structural and Spectroscopic Evidence for Molybdenum-to-Bipyridyl π* Bonding

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During the course of work aimed at preparing compounds related to $Mo(OBu\text{-}t)_2(py)_2(CO)_2$,[1] we discovered that hydrocarbon solutions of $Mo_2(OPr\text{-}i)_6$[2] (M≡M) and bpy (2,2′-bipyridine) react[3] to give deep-purple solutions from which crystals of $Mo(OPr\text{-}i)_2(bpy)_2$ are obtained in near quantitative yield, based on reaction 1.

$$Mo_2(OPr\text{-}i)_6 + 2bpy \rightarrow Mo(OPr\text{-}i)_2(bpy)_2 + {}^1/_2Mo_2(OPr\text{-}i)_8 \quad (1)$$

The cleavage of the Mo≡Mo bond is noteworthy since monodentate ligands, such as pyridine, are known to form adducts of the type $Mo_2(OR)_6L_2$ with retention of the triple bond.[4]

$Mo(OPr\text{-}i)_2(bpy)_2$ is an air-sensitive, paramagnetic, dark-purple crystalline solid, sparingly soluble in alkane solvents, but very soluble in benzene and toluene. Its color is derived from an intense band at $\lambda_{max}$ 530 nm ($\epsilon$ 10 000).

The molecular structure in the solid state revealed[5] a distorted octahedral geometry for the central $MoO_2N_4$ skeleton. An ORTEP view of the molecule is shown in Figure 1, and pertinent distances and angles associated with the central $MoO_2N_4$ skeleton are given in Table I. The Mo–O distances are short, comparable to those in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$, which implies significant oxygen-p-to-molybdenum-d π bonding. The alkoxy ligands, however, are cis in $Mo(OPr\text{-}i)_2(bpy)_2$ and trans in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$. The Mo–N distances in $Mo(OPr\text{-}i)_2(bpy)_2$ are short, 2.12 Å (average), which may be compared to Mo–N = 2.35 Å (average) in $Mo(OBu\text{-}t)_2(py)_2(CO)_2$.

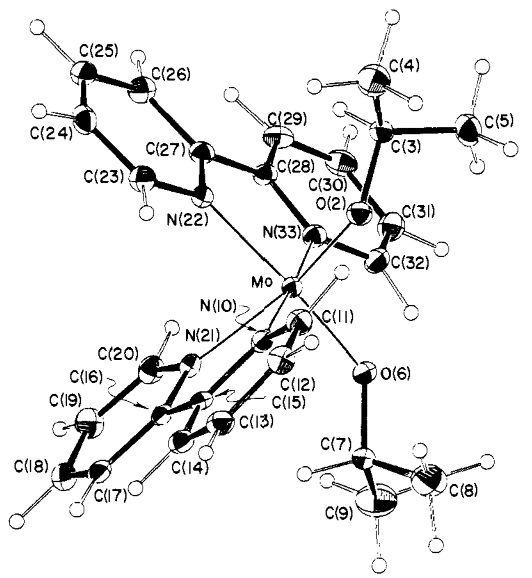

**Figure 1.** ORTEP view of the $Mo(OPr\text{-}i)_2(bpy)_2$ molecule showing the atom numbering scheme used in the tables.

Table I. Bond Distances (Å) and Angles (Deg) Associated with the Central $MoO_2N_4$ Skeleton of the $Mo(OPr\text{-}i)_2(bpy)_2$ Molecule

| A | B | dist |
|---|---|---|
| Mo(1) | O(2) | 1.942 (2) |
| Mo(1) | O(6) | 1.932 (2) |
| Mo(1) | N(10) | 2.107 (2) |
| Mo(1) | N(21) | 2.123 (2) |
| Mo(1) | N(22) | 2.126 (2) |
| Mo(1) | N(33) | 2.115 (2) |

| A | B | C | angle |
|---|---|---|---|
| O(2) | Mo(1) | O(6) | 105.3 (1) |
| O(2) | Mo(1) | N(10) | 85.1 (1) |
| O(2) | Mo(1) | N(21) | 155.4 (1) |
| O(2) | Mo(1) | N(22) | 91.6 (1) |
| O(2) | Mo(1) | N(33) | 97.9 (1) |
| O(6) | Mo(1) | N(10) | 97.0 (1) |
| O(6) | Mo(1) | N(21) | 90.2 (1) |
| O(6) | Mo(1) | N(22) | 153.7 (1) |
| O(6) | Mo(1) | N(33) | 84.3 (1) |
| N(10) | Mo(1) | N(21) | 73.9 (1) |
| N(10) | Mo(1) | N(22) | 104.5 (1) |
| N(10) | Mo(1) | N(33) | 176.2 (1) |
| N(21) | Mo(1) | N(22) | 81.6 (1) |
| N(21) | Mo(1) | N(33) | 102.6 (1) |
| N(22) | Mo(1) | N(33) | 73.3 (1) |

A close inspection of the interatomic distances associated with the bpy ligands revealed small but systematic deviations from those distances found in either the free ligand[6] or any of its structurally characterized coordination compounds involving the transition elements.[7] This observation prompted us to redetermine the structure of 2,2′-bipyridine[8] in order to make a more accurate

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(1) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7615.

(2) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(3) Standard procedures for the manipulation of air-sensitive samples were employed throughout. All solvents were dried and deoxygenated.

(4) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153.

(5) Crystal data obtained for $Mo(OPr\text{-}i)_2(bpy)_2$ collected at −165 °C: space group $P\bar{1}$, with $a$ = 12.677 (2), $b$ = 12.885 (2), $c$ = 8.763 (1) Å; $\alpha$ = 66.32 (1), $\beta$ = 107.29 (1), $\gamma$ = 111.28 (1)°; $Z$ = 2; $d_{calcd}$ = 1.455 g cm$^{-3}$. Of the 4257 unique structure amplitudes, the 3895 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R(F)$ = 0.0314 and $Rw(F)$ = 0.0357.

(6) Merritt, L. L.; Schroeder, E. D. *Acta Crystallogr.* **1956**, *9*, 801.

(7) For structure of Mo–bpy-containing compounds, see: (a) $Mo(CO)_3(py)(bpy)$: Griffiths, A. *J. Cryst. Mol. Struct.* **1971**, *1*, 75. (b) $MoO_2Br_2(bpy)$: Fenn, R. H. *J. Chem. Soc. A* **1969**, 1764. (c) $Mo(CO)_3(bpy)(\mu\text{-}Cl)SnCl_2Me$: Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1268. (d) $Mo(CO)_2(CNS)(\eta^3\text{-}C_3H_5)(bpy)$: Graham, A. J.; Fenn, R. H. *J. Organomet. Chem.* **1969**, *17*, 405. (e) $Mo(CO)_2(\eta^3\text{-}C_3H_5)(py)(bpy)BF_4$: Fenn, R. H.; Graham, A. J. *Ibid.* **1972**, *37*, 137. (f) $[Mo(bpy)O(HOPO_2)]_2(\mu\text{-}O)_2$: *Acta Crystallogr., Sect. B* **1976**, *32*, 2627.

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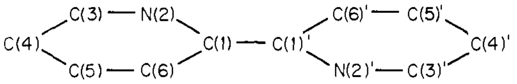
Table II. Comparison of the Interatomic Bond Distances (Å) in 2,2′-Bipyridine with Those Found in the Coordinated 2,2′-Bipyridyl Ligands in $Mo(OPr\text{-}i)_2(bpy)_2$[a]

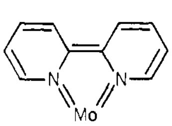


| A | B | dist | A | B | dist | A | B | dist |
|---|---|---|---|---|---|---|---|---|
| C(1) | N(2) | 1.346 (2) | C(15) | N(10) | 1.388 (4) | C(27) | N(22) | 1.370 (4) |
| N(2) | C(3) | 1.341 (2) | N(10) | C(11) | 1.375 (4) | N(22) | C(23) | 1.373 (4) |
| C(3) | C(4) | 1.384 (2) | C(11) | C(12) | 1.357 (4) | C(23) | C(24) | 1.357 (4) |
| C(4) | C(5) | 1.383 (3) | C(12) | C(13) | 1.418 (4) | C(24) | C(25) | 1.417 (5) |
| C(5) | C(6) | 1.385 (2) | C(13) | C(14) | 1.367 (4) | C(25) | C(26) | 1.371 (5) |
| C(6) | C(1) | 1.394 (2) | C(14) | C(15) | 1.405 (4) | C(26) | C(27) | 1.412 (4) |
| C(1) | C(1)′ | 1.490 (3) | C(15) | C(16) | 1.425 (4) | C(28) | C(27) | 1.424 (4) |
| C(1)′ | N(2)′ | 1.346 (2) | C(16) | N(21) | 1.381 (4) | C(27) | N(22) | 1.370 (4) |
| N(2)′ | C(3)′ | 1.341 (2) | N(21) | C(20) | 1.376 (4) | N(22) | C(23) | 1.373 (4) |
| C(3)′ | C(4)′ | 1.384 (2) | C(20) | C(19) | 1.359 (4) | C(23) | C(24) | 1.357 (4) |
| C(4)′ | C(5)′ | 1.383 (3) | C(19) | C(18) | 1.413 (5) | C(24) | C(25) | 1.417 (5) |
| C(5)′ | C(6)′ | 1.385 (2) | C(18) | C(17) | 1.358 (4) | C(25) | C(26) | 1.371 (5) |
| C(6)′ | C(1)′ | 1.394 (2) | C(17) | C(16) | 1.414 (4) | C(26) | C(27) | 1.412 (4) |

[a] The atom numbering scheme for 2,2′-bipyridine is shown here, while that for the coordinated ligand is shown in Figure 1.

comparison of the interatomic distances. These are shown in Table II.

The structural data may be taken as evidence for a significant bonding contribution of the resonance form shown below. In a



molecular orbital description, this is equivalent to Mo-d-to-bpy $\pi^*$ bonding with extensive electron population of the lowest unoccupied molecular orbital [$b_1(\pi^*)$] of the 2,2′-bipyridine.

Solutions of $Mo(OPr\text{-}i)_2(bpy)_2$ were examined by resonance Raman (RR) spectroscopy to determine whether the unusual structural characteristics of the compound are evident spectroscopically and whether conclusions may be drawn regarding the extent of $\pi$ back-bonding. The RR spectra of bpy complexes typically show[9,10] seven strong peaks in the frequency range 1000–1700 $cm^{-1}$, corresponding, essentially, to the seven symmetric C–C and C–N stretches of bpy in any point group for which the two pyridine rings are related by a symmetry element. In addition, four symmetric in-plane C–H wags are expected in this frequency region, and these are sometimes observed as weak features.[10] As can be seen in Table III,[11] the RR spectra of $Ru(bpy)_2(NH_3)_2^{2+}$, $Ru(bpy)_2Cl_2$, and $Li^+(bpy^-\cdot)$ exhibit essentially this typical pattern of seven strong, polarized bands, although the RR mode near 1040 $cm^{-1}$ in $Ru(bpy)_2Cl_2$ is very weak and $Li^+(bpy^-\cdot)$ has an "extra" peak at 1351 $cm^{-1}$. The latter must reflect contribution by C–H wag to the obsd. RR modes of the radical. The time-resolved RR spectrum of the metal-to-ligand charge-transfer (MLCT) excited state of $Ru(bpy)_3^{2+}$ appears more complex because it is actually the superimposition of neutral and radical-like bipyridine spectra, $Ru^{III}(bpy)_2(bpy)^-\cdot$, and therefore may be separated into two seven-peak patterns.[9,12] It can also be seen from the data in Table III that the bpy ring stretching frequencies respond in a predictable way to $\pi$-antibonding electron density: $bpy^-\cdot$ and the "radical-like" ligand of the MLCT excited state of $Ru(bpy)_3^{2+}$ exhibit frequencies approximately 60 $cm^{-1}$ lower than those in $Ru(bpy)_2(NH_3)_2^{2+}$, $Ru(bpy)_2Cl_2$, and the "neutral" ligands in the MLCT excited state of $Ru(bpy)_3^{2+}$.

Table III. Resonance Raman Frequencies ($cm^{-1}$) of $C_2$ Bipyridine Complexes and Bipyridine Radical Anion

| $Ru(bpy)_2\cdot(NH_3)_2^{2+}$ | $Ru(bpy)_2\text{-}Cl_2$ | $Mo(bpy)_2\text{-}(OPr\text{-}i)_2$ | MLCT state[a] of $Ru(bpy)_3^{2+}$ | $Li^+\text{-}(bpy^-\cdot)$[b] |
|---|---|---|---|---|
| 1607 | 1603 | 1590* | 1609, 1550 | 1554 |
| 1561 | 1554 | 1526*, 1515 | 1566, 1482 | 1486 |
| 1490 | 1484 | 1457*, 1441 | 1500, 1429 | 1412 |
| | | 1354, 1363 (vw) | 1370 | 1351 |
| 1320 | 1316 | 1304*, 1278 | 1324, 1288 | 1275 |
| 1273 | 1268 | 1255*, 1233 | . . ., 1214 | 1206 |
| 1172 | 1166 | 1163, 1029[c] | 1176, 1035[c] | 1019 |
| 1038 | | 1093, 1011[c] | 1044, 1016[c] | 992 |
| | | 785, 763 (vw) | 744 | 744 |
| 672 | 669 | 659, 624 | | 646 |
| 375 | 376 | 376 | 384, 340 | 308 |

[a] The structure of this excited state is approximately characterized as $Ru^{III}(bpy)_2(bpy^-\cdot)^{2+}$. See: Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* 1979, *101*, 4391. [b] Woodruff, W. H.; Hornberger, B., manuscript in preparation. Hornberger, B. M. S. Thesis, The University of Texas at Austin, 1980. [c] Frequency correlations involving $Mo(bpy)_2(OPr\text{-}i)_2$ and the excited state of $Ru(bpy)_3^{2+}$ in this region are tentative. Asterisk indicates frequencies used in $\pi^*$ electron density calculation. See text.

The RR spectrum for $Mo(OPr\text{-}i)_2(bpy)_2$ is remarkable in two respects. First, the spectrum is complex, and second, the clearly identifiable bpy modes are shifted to considerably lower frequencies relative to the neutral bpy ligands, although not to frequencies as low as those of $bpy^-\cdot$.

The origin of the complexity of the spectrum is presently uncertain. One plausible explanation lies in the fact that the highest symmetry assignable to $Mo(OPr\text{-}i)_2(bpy)_2$ is $C_2$. In this point group, the two pyridine rings of each bpy are inequivalent and 13, rather than 7, symmetric stretching modes may be observed. That this effect is apparent in $Mo(OPr\text{-}i)_2(bpy)_2$ and not in other *cis*-$MX_2(bpy)_2$ complexes may be ascribed to the strong $\pi$-donor influence of the OPr-*i* ligands. In any event, the shift to lower frequencies of the bpy bands in $Mo(OPr\text{-}i)_2(bpy)_2$ is clearly ev-

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(8) Crystal data for 2,2′-bipyridine obtained at ·163 °C from 34 reflections by using Mo Kα radiation (λ 0.71069 Å): space group $P2_1/c$, $a = 5.485$ (1), $b = 6.177$ (1), $c = 12.356$ (4) Å; $\beta = 110.83$ (1)°; $Z = 2$; $d_{calcd} = 1.326$ g $cm^{-1}$. Of the 1154 unique structure amplitudes, the 884 having $F > 2.33\sigma(F)$ were used in the full matrix refinement. Final residuals $R(F) = 0.058$ and $Rw(F) = 0.067$.

(9) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.

(10) Clark, R. J. H.; Turtle, P. C.; Strummen, D. P.; Strensand, B.; Kincaid, J.; Nakamoto, K. *Inorg. Chem.* **1977**, *16*, 84.

(11) Resonance Raman spectra were obtained by using a SPEX Ramalog EU spectrometer with an RCA C31034A PMT and an ORTEC 9300 series photon counter. The experimental setup for the excited state $Ru(bpy)_3^{2+}$ spectroscopy is described elsewhere.[9] Spectra of the Mo(II) and Ru(II) complexes were obtained by using $Ar^+$ laser excitation at 457.9 nm (Ru), 488.0 nm (Ru, Mo), and 514.5 nm (Mo). Bipyridine radical anion spectra were excited by using the above wavelengths and, in addition, 363.8 nm ($Ar^{2+}$ line). Solvents and concentrations employed were $H_2O$ [$Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(NH)_2^{2+}$, $\sim 10^{-4}$ M], $CH_2Cl_2$ [$Ru(bpy)_2Cl_2$, $\sim 10^{-4}$ M], and THF [$Mo(bpy)_2(i\text{-}PrO)_2$, $\sim 10^{-3}$ M; $Li^+(bpy^-\cdot)$, $10^{-3}$–$10^{-4}$ M].

(12) Bradley, P. G.; Kress, N.; Dallinger, R. F.; Woodruff, W. H., Hornberger, B. A. *J. Am. Chem. Soc.*, in press.

idence for $\pi$-electron donation from $Mo(OPr\text{-}i)_2$ to the antibonding orbitals of the bpy ligands. The extent of this back-donation can be calculated quantitatively from the bpy vibrational frequencies, but justification of such a calculation is beyond the scope of this communication. Qualitatively, the RR frequencies are consistent with a net negative charge of approximately 0.5 $e^-$ in the lowest $\pi$* orbitals of each bpy in $Mo(OPr\text{-}i)_2(bpy)_2$.

We conclude that the $Mo(OR)_2$ moiety is a most unusually powerful $\pi$ donor, even to ligands like 2,2′-bipyridine which do not normally act as $\pi$-acceptor ligands in the ground state. The only other transition-metal complexes which are perhaps analogous to $Mo(OPr\text{-}i)_2(bpy)_2$ are the 1,4-diimine adducts of $Cp_2Ti$ and $Cp_2Zr$, studied by Stucky and his co-workers.[13,14]

**Acknowledgment.** We thank the National Science Foundation, donors of the Petroleum Research Fund, administered by the American Chemical Society, and Marshal H. Wrubel Computing Center for support at Indiana University and the National Science Foundation and Robert A. Welch Foundation for support at the University of Texas.

**Supplementary Material Available:** Fractional coordinates and isotropic and anisotropic thermal parameters for $Mo(OPr\text{-}i)_2(bpy)_2$ and 2,2′-bipyridine (5 pages). Ordering information is given on any current masthead page.

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[13] McPherson, A. M.; Fieselmann, B. F.; Lichtenberger, D. L.; McPherson, G. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 3425.

[14] Corbin, D. R.; Willis, W. S.; Duesler, E. N.; Stucky, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 5969.

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## A Semichelating Metal-$\beta$-Diketonate Complex

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*Received January 22, 1981*

Comprehensive investigations of the isomerization process in octahedral metal-$\beta$-diketone complexes have revealed two limiting mechanistic pathways which may be distinguished by the effective coordination number of the metal in the transition state. They are (1) twist mechanisms, in which chemical bonds are not broken, and (2) bond rupture pathways which lead to idealized square-pyramidal or trigonal-bipyramidal intermediates with "dangling" axial or equatorial ligands.[1-3] We wish to report the synthesis of a new compound whose structure and NMR spectra reveal novel bonding features like those proposed for the dangling ligand in bond rupture isomerizations or, alternatively, in substitution processes in square planar complexes.

Reaction of the tridentate phosphine $Ph_2PC_2H_4P(Ph)C_2H_4PPh_2$ (triphos) with palladium bis(hexafluoroacetylacetonate) [Pd($F_6$acac)$_2$] in benzene affords the 1:1 adduct (triphos)Pd($F_6$acac)$_2$ (**1**), mp 192 °C; $^{31}P$ NMR $\delta$ 108.2 (d) and 48.6 (t, $J_{PP}$ = 9.5 Hz).[4] Crystals suitable for X-ray diffraction experiments were grown by slow evaporation of an ethanol solution.[5]

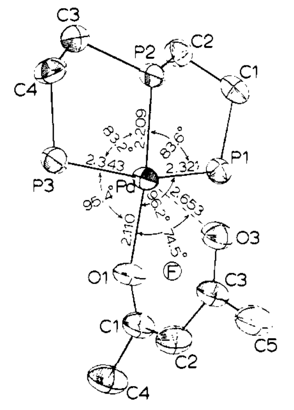

**Figure 1.** Coordination core of (triphos)Pd($F_6$acac)$_2^+$.

The solid-state structure of **1** contains two types of hexafluoroacetylacetonate groups. One is not bonded to the metal and corresponds to ionic $F_6$ acac$^-$. The other is attached to palladium by a normal 2.110 (5) Å Pd–O bond as shown in Figure 1, which depicts the coordination core of the metal. The other three coordination sites are occupied by phosphorus atoms from the triphos. The palladium atom is displaced by 0.22 Å in the direction of O(3) from the weighted least-squares plane containing P(1), P(2), P(3), and O(1). A novel feature of the bonding in (triphos)Pd($F_6$acac)$_2$ involves O(3), the other terminus of the coordinated $F_6$acac group. This ligand, which is planar within experimental error, is positioned so that its plane makes a dihedral angle of 85.4° with the $P_3$OPd plane. In this conformation, O(3) lies above the palladium atom in an axial position. The resulting Pd–O contact, 2.653 (6) Å, is rather long, and it presumably represents a weakly bonding interaction so that the overall coordination geometry is described as distorted square pyramidal. The principal distortion is due to the small "bite" angle of the $F_6$acac ligand [O(1)–Pd–O(3), 74.5 (4)°] which places O(3) slightly off of the ideal axial position. The O(3)–Pd–P equatorial angles reflect this: O(3)–Pd–P(1), 97.5; O(3)–Pd–P(2), 113.8; O(3)–Pd–P(2), 97.4°. The weakly bonding axial Pd–O interaction is much shorter than the 3.1-Å axial Pd–O contact observed in Pd($F_6$acac)$_2$·(4-$ClC_5H_4N)_4$.[6] A much less drastic distortion in another $F_6$acac complex, (bpy)Cu($F_6$acac)$_2$, has been proposed to arise from a Jahn–Teller effect, but the longer Cu–O bond was 2.296 (4) Å.[7]

Variable-temperature NMR spectroscopy revealed two dynamic processes in **1**. The $^{19}F$ NMR spectrum of (triphos)Pd($F_6$acac)$_2$ in $CD_2Cl_2$ at −64 °C demonstrated three singlets in a 1:2:1 ratio at 75.44, 76.08, and 77.24 ppm. The center field resonance is assigned, on the basis of its chemical shift and relative intensity, to the ionic $F_6$acac. On warming, these three signals coalesced into a single broad peak. These data indicate that there is a facile exchange between ionic and coordinated $F_6$acac; $\Delta H_{acl}$ for this process was found to be 6 kcal mol$^{-1}$ and $\Delta S_{acl}$ to be −26 eu.[4]

The coordinated $F_6$acac ligand is itself fluxional. Variable-temperature $^{19}F$ NMR spectra of [(triphos)Pd($F_6$acac)]$BPh_4$ (**2**) prepared by metathesis of **1** with sodium tetraphenylborate in methanol, showed that the two types of $CF_3$ groups rapidly interconvert on the NMR time scale. The limiting low-temperature spectrum, obtained at −11 °C, showed two fluorine resonances at 75.75 and 77.86 ppm. The activation enthalpy for this second process, measured for a $5 \times 10^{-2}$ M solution in 1,2-dichloroethane, was 8.1 ± 1 kcal mol$^{-1}$ with $\Delta S_{acl}$ −21 ± 3 eu. Since the reaction rates, as reflected by the NMR line shapes, are the same at both $5 \times 10^{-2}$ and $7 \times 10^{-3}$ M concentrations, it is probable that the exchange is intramolecular.

Rapid exchange of the two inequivalent ends of an acetylacetonate group has been observed, for example, in the silicon enol complexes $R_3Si$(acac).[8] In sulfur chelates, fluxional behavior

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967, pp 300–334.

[2] N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).

[3] L. H. Pignolet, *Top. Curr. Chem.*, **56**, 93 (1975).

[4] $^{31}P$ and $^{19}F$ NMR chemical shifts are with respect to external 85% $H_3PO_4$ or internal $CFCl_3$.

[5] X-ray diffraction data: crystal system orthorhombic; space group *Pna2*$_1$; $a$ = 31.120 (7), $b$ = 14.690 (3), $c$ = 10.037 (2) Å; V = 4589 Å$^3$; Z = 4; density = 1.527 g cm$^{23}$; diffractometer = Enraf–Nonius CAD 4; radiation = graphite monochromatized Mo K$\alpha$; scan range 0° ≤ $2\theta$ ≤ 50°; reflections collected = 4765 total unique, 3330 observed with $F_o^2 > 2.0\sigma(F_o^2)$; $R$ = 0.049 and $R_W$ = 0.066. by full·matrix least-squares refinement.

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