

## REACTIONS OF COORDINATED MOLECULES

### XVII \*. A SPECTROSCOPIC STUDY OF THE STRUCTURE AND BONDING OF SEVERAL METALLA- $\beta$ -DIKETONE MOLECULES AND COMPLEXES WITH ALUMINUM AND BORON

KEVIN P. DARST and C.M. LUKEHART \*

*Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235 (U.S.A.)*

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#### Summary

The  $^{13}\text{C}$  NMR spectra of 12 complexes which contain a metalla- $\beta$ -diketone moiety and of 7 reference compounds are reported. The 12 metalla- $\beta$ -diketone compounds consist of two enol tautomers, six metalla- $\beta$ -diketonate complexes of boron and four tris(metalla- $\beta$ -diketonate)aluminum complexes. These spectral data provide a diagnostic indication of the formation of metalla- $\beta$ -diketone compounds, a convenient and direct comparison of these metalla molecules to the organic analogues and a sensitive probe for determining the solution-phase molecular structures of these complexes. The  $^{19}\text{F}$  NMR spectra of two of these molecules are reported, also.

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#### Introduction

We reported recently the preparation of several metalla- $\beta$ -diketone molecules including the rhenium molecules (A) where R is methyl, isopropyl or benzyl [2]. These complexes are metalla analogues of the enol tautomers of  $\beta$ -diketone molecules where the methine group is formally substituted by the metal complex. The metalla- $\beta$ -diketone molecules will react with a variety of trigonal boron compounds to give the neutral metalla- $\beta$ -diketonate complexes (B) [3,4]. This reaction parallels the reaction of acetylacetone with  $\text{BF}_3$  affording the (acetylacetonate) $\text{BF}_2$  complex.

The coordination of the metalla- $\beta$ -diketonate anions to both main group and transition metal ions demonstrates another similarity between these anions and the organic analogues [2,5,6]. In these complexes, such as the aluminum com-

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\* For Part XVI see ref. 1.



resonances are provided in the Experimental. The  $^{13}\text{C}$  spectra of 10 particularly relevant metalla- $\beta$ -diketone complexes are shown in Fig. 1. The following discussion will summarize only the significant features of these spectra.

#### *The acyl complexes*

The  $^{13}\text{C}$  NMR spectra of the four acylpentacarbonyl complexes (I–IV) are reported as reference spectra. The methyl- and acyl-carbon resonances of the acetyl-manganese and -rhenium complexes I and II differ by only 4.1 and 2.1 ppm, respectively. The average chemical shift of the acyl-carbon nuclei is  $\delta$  254.0 ppm. However, the carbonyl-carbon resonance of the manganese complex (I) appears at 22.4 ppm to lower field than the weighted-average chemical shift of the two carbonyl-carbon resonances of the rhenium complex (II). This shift may reflect the higher electron density about the rhenium atom.

The three acylpentacarbonylrhenium complexes (II–IV) show two carbonyl-carbon resonances which have an average splitting of 2.1 ppm. The resonance at lower field is nearly four times as intense as the higher-field resonance, and these resonances are assigned to the *cis* and *trans* carbonyl ligands, respectively. As the number of carbon atoms within the acyl ligand increases the chemical shift of the  $\alpha$ -carbon atom decreases from  $\delta$  56.7 to 75.5 ppm, the chemical shift of the acyl-carbon atom increases from  $\delta$  252.9 to 246.6 ppm, and the weighted-average chemical shift of the carbonyl carbon nuclei increases slightly from  $\delta$  187.6 to 183.4 ppm.

#### *The metalla- $\beta$ -diketone molecules*

The  $^{13}\text{C}$  NMR spectra of acetylacetone (V) and the metalla-acetylacetone molecule (VI, 3,3,3,3-tetracarbonyl-3- $\lambda^6$ -rhenia-2,4-pentanedione) reveal the effect of substituting the methine group by the organometallic complex. Only the resonances of the enol tautomer of acetylacetone are used in this comparison since the metalla- $\beta$ -diketone molecules exist only as the enol tautomer. Both the methyl- and acyl-carbon resonances of VI appear at much lower field than the corresponding resonances of acetylacetone. These shifts are 28.8 and 106.0 ppm, respectively. Although the distinction between the diamagnetic and paramagnetic contributions to the  $^{13}\text{C}$  chemical shift is not easily made, the high electronegativity of the  $\text{Re}(\text{CO})_4$  moiety may account for most of this shift.

The  $^{13}\text{C}$  NMR spectrum of the metalla-5-methylhexane-2,4-dione complex (VII) can be interpreted readily. The resonance of the methine carbon atom appears at  $\delta$  61.3 ppm. The two acyl-carbon resonances at  $\delta$  297.4 and 304.1 ppm are assigned to the acetyl and isobutyryl fragments, respectively. Although VI has two carbonyl-carbon resonances of nearly equal intensity at  $\delta$  188.0 and 191.1 ppm, complex VII has one carbonyl-carbon resonance at  $\delta$  188.2 ppm and two other resonances of essentially one half the relative intensity at  $\delta$  190.8 and 191.5 ppm. Clearly, the  $C_{2v}$  symmetry of VI and the  $C_s$  symmetry of VII confirm the assignment of the axial carbonyl-carbon atoms to the resonance at ca.  $\delta$  188 ppm and the equatorial carbonyl-carbon atoms to the resonance at ca.  $\delta$  191 ppm. The average separation between the axial and equatorial carbonyl-carbon resonances is 3.0 ppm, and the anisochronism of the nonequivalent equatorial carbonyl-carbon atoms in VII is 0.7 ppm.

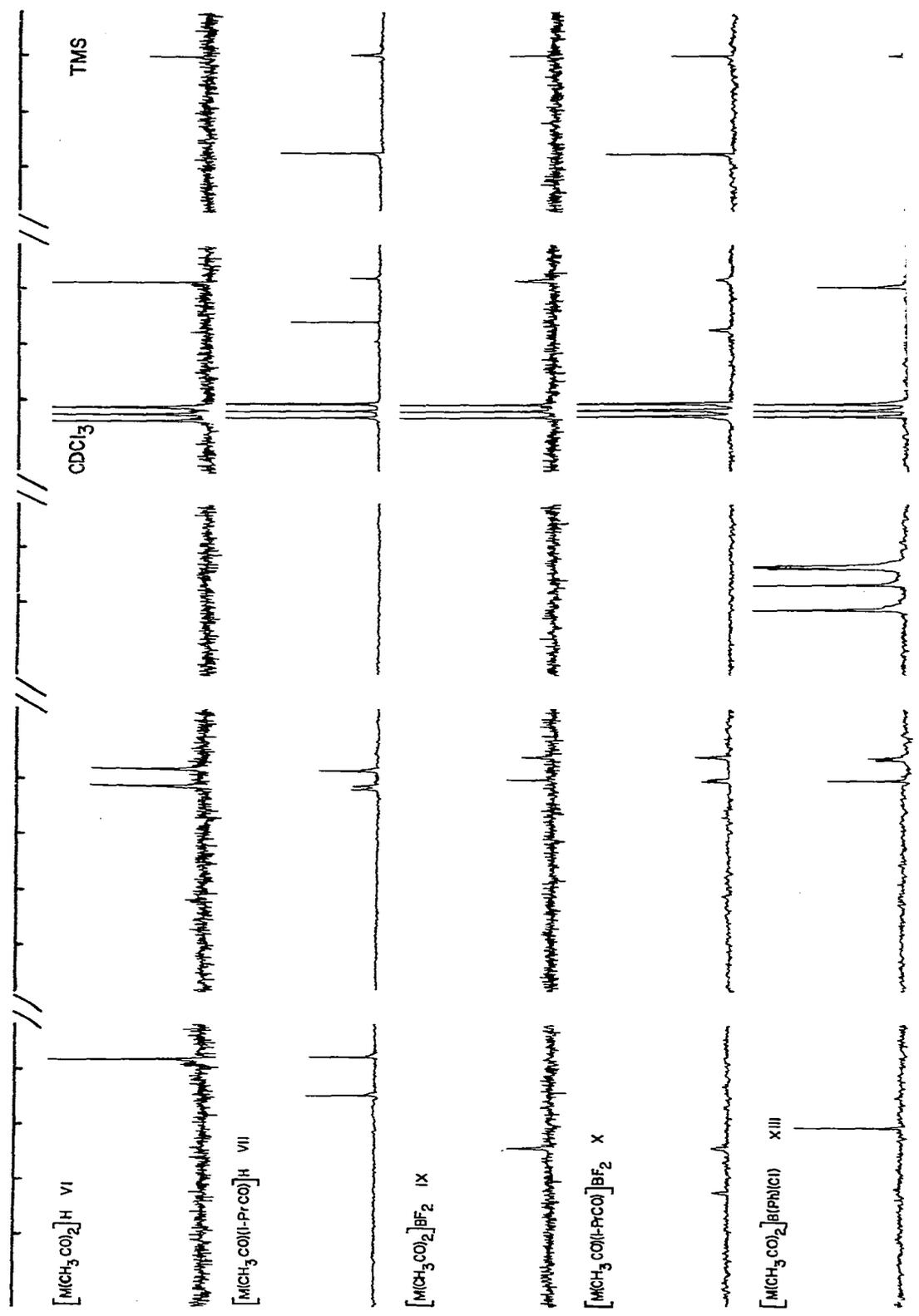




Fig. 1. The  $^{13}C$  NMR spectra of two metal- $\beta$ -diketone molecules VI and VII, four metal- $\beta$ -diketonate complexes of boron (IX, X, XIII and XIV), and four metal- $\beta$ -diketonate complexes of aluminum (XVI–XIX), where M is *cis*-(OC) $_4$ Re and M' is *cis*-(OC) $_4$ Mn. The solvent resonances appear as three singlets centered at  $\delta$  77.2 ppm.

In going from the acyl complexes II and III to the metalla- $\beta$ -diketone molecules VI and VII the acetyl-methyl- and methine-carbon resonances each shift upfield by 3.3 ppm, the weighted-average carbonyl carbon resonances shift downfield by 2.0 and 5.7 ppm, and the acyl-carbon resonances shift downfield by 44.7 and 50.1 ppm, respectively. These shifts indicate only a slight change in charge at the Re atoms, and a significant increase in positive charge at the acyl-carbon atoms. The acyl-carbon resonances of VI and VII appear approximately midway between the resonance of the corresponding carbon atom in the acyl complex and the resonance of the carbenoid carbon atom in the (hydroxy)(methyl)carbenoid complex,  $(OC)_5W[C(OH)(CH_3)]$ , which appears at  $\delta$  334.4 ppm [12]. This result is not unexpected when considering the two principal resonance forms for these metallaenol tautomers (A).

#### *The metalla- $\beta$ -diketonate complexes of boron*

The methyl- and acyl-carbon resonances of (acetylacetonate)BF<sub>2</sub> (VIII) are shifted downfield by 29.8 and 120.4 ppm, respectively, in going to the (metallaacetylacetonate)BF<sub>2</sub> complex (IX). Similar shifts are observed between acetylacetonate (V) and the metalla analogue (VI) and are due, presumably, to the substitution of the electronegative Re(CO)<sub>4</sub> moiety for the methine group.

When the metallaacetylacetonate (VI) and metalla-5-methylhexane-2,4-dione (VII) molecules are converted into the corresponding BF<sub>2</sub> complexes (IX and X), the weighted-average carbonyl carbon resonances shift to higher field by only 1.9 ppm. However, the average acyl-carbon resonances shift downfield by 16.1 and 17.1 ppm, respectively. Apparently the highly electronegative BF<sub>2</sub> groups draw considerable electron density from the acyl carbon atoms without a corresponding donation of electron density from the rhenium atom. In contrast, the resonance of the acyl-carbon atom in (acetylacetonate)BF<sub>2</sub> shifts only 1.7 ppm to lower field from the acyl-carbon resonance of the enol tautomer of acetylacetonate. An equivalent shift of the methine-carbon resonances is observed. These unusually large shifts in the metalla complexes apparently reflect the high electronegativity of the Re(CO)<sub>4</sub> moiety and the lesser degree of electron delocalization within the metalla- $\beta$ -diketonate ligand.

The <sup>13</sup>C NMR spectra of the BCl<sub>2</sub> (XI) and BF<sub>2</sub> (IX) metallaacetylacetonate complexes are not significantly different. The organic analogue of XI is not known. The spectra of the (metalla-1-phenylpentane-2,4-dionate)BF<sub>2</sub> complex (XII) and the (metalla- $\beta$ -diketonate)B(C<sub>6</sub>H<sub>5</sub>)(Cl) complexes (XII–XIV) can be interpreted readily. However, the spectra of IX, X, XIII and XIV are shown in Fig. 1 since the observed symmetry-imposed variations indicate a molecular structure of type B and permit the unambiguous assignment of the acyl- and carbonyl-carbon resonances.

Complex IX has C<sub>2v</sub> symmetry and shows two carbonyl-carbon resonances at  $\delta$  185.6 and 189.7 ppm and a single acyl-carbon resonance at  $\delta$  314.0 ppm. Complex X has C<sub>s</sub> symmetry where the axial carbonyl ligands are equivalent. These carbon atoms appear as a singlet at  $\delta$  185.7 ppm, while the nonequivalent equatorial carbonyl-carbon atoms appear as two singlets of lower intensity at  $\delta$  190.1 and 189.7 ppm. The axial–equatorial anisochronism is 4.2 ppm, and the equatorial–equatorial anisochronism is 0.4 ppm [13]. Similarly, the two acyl-carbon atoms are nonequivalent, and the two resonances at  $\delta$  313.9

and 321.9 ppm are assigned readily to the acetyl- and isobutyryl-acyl carbon atoms, respectively.

Complex XIII also possesses  $C_s$  symmetry, but now the axial carbonyl ligands are nonequivalent while the two equatorial carbonyl ligands and the two acyl-carbon atoms are equivalent. The axial carbonyl carbon resonance appears as two singlets separated by 0.4 ppm at  $\delta$  186.4 and 186.0 ppm, and the equatorial carbonyl-carbon resonance appears as a more intense singlet at slightly lower field ( $\delta$  190.0 ppm). The singlet for the acyl carbon atoms appears at  $\delta$  310.5 ppm.

The asymmetry of XIV is reflected in the  $^{13}\text{C}$  NMR spectrum. The carbonyl-carbon atoms appear as 4 singlets centered at  $\delta$  188.0 ppm. The pair of resonances at higher field are assigned to the axial carbonyl ligands, and the pair of resonances at lower field are assigned to the equatorial carbonyl-carbon atoms. The axial-equatorial separation is 3.8 ppm, and the average anisochronism within each set of carbonyl ligands is 0.3 ppm. Two acyl-carbon resonances are observed as expected. These resonances appear at  $\delta$  310.0 and 317.7 ppm and are assigned readily to the acetyl and isobutyryl fragments, respectively.

#### *The metalla- $\beta$ -diketonate complexes of aluminum*

The methyl- and acyl-carbon resonances of tris(acetylacetonate)aluminum (XV) are shifted to lower field in the manganese and rhenium metalla analogues (XVI and XVII). The average shifts are 29.7 ppm for the methyl carbon atoms and 120.9 ppm for the acyl carbon atoms. The large shift of the acyl resonance to lower field is particularly characteristic of the metalla- $\beta$ -diketonate complexes, and, presumably, reflects the high electronegativity of the carbonylmetal moiety.

When the acetylpentacarbonyl-manganese and -rhenium complexes (I and II) are converted into the aluminum metallaacetylacetonate complexes (XVI and XVII), the methyl- and carbonyl-carbon resonances shift slightly to lower field while the acyl-carbon resonances shift to lower field by 70.8 and 48.1 ppm, respectively. Presumably, the more electron-rich rhenium atom can stabilize a positive charge on the acyl-carbon atoms better than manganese.

The molecular structures of XVI and the rhenium metallaacetylacetonate complex (VI), reveal that the axial carbonyl ligands of XVI are tilted more toward the metalla-chelate ring than those of VI [8,7]. This tilting may arise from an intramolecular synergistic  $\pi$ -bonding interaction between the axial carbonyl ligands and the metalla- $\beta$ -diketone  $\pi$ -electron system [9]. A recent force-constant calculation indicates that the axial and equatorial carbonyl ligands are more non-equivalent in XVI than in VI which is consistent with such an interaction [14].

The  $^{13}\text{C}$  NMR spectra may reflect this difference, also. As the axial carbonyl tilting increases, these ligands become more dissimilar to the equatorial carbonyl ligands and the anisochronism between these two sets of carbonyl ligands should increase. The axial-equatorial carbonyl ligand anisochronism is 5.3 and 3.1 ppm in XVI and VI, respectively, which fits the expected trend. However, this correlation may be fortuitous since the corresponding anisochronism in XVII of only 1.6 ppm indicates little or no interaction between the axial carbonyl ligands and the metalla-chelate ring. This result is not consistent with

the force-constant data, although an X-ray structure determination of XVII has not been performed. Further direct structural information may resolve this ambiguity.

The effect of the central coordinating species is evident from the spectra of the rhenium metallaacetylacetonate complex (XVII), the rhenium metallaacetylacetonate molecule (VI) and the corresponding  $\text{BF}_2$  complex (IX). Although the average carbonyl carbon resonances for these complexes appear over only 3.0 ppm range, the position of the acyl-carbon resonance varies with the type of complex. This resonance shifted from  $\delta$  297.9 ppm for VI to  $\delta$  301.0 ppm for XVII and to  $\delta$  314.0 ppm for IX which parallels the expected electronegativity of the central coordinating atom. Also, the methyl-carbon resonance of the aluminum complex (XVII) appears at 4.6 ppm below the average methyl-carbon resonance for VI and IX. This unusual shift may reflect the more extensive delocalization within the metalla-chelate ring of XVII because of the available  $3d$  orbitals of the aluminum atom.

The compounds XVIII and XIX are tris-chelate complexes of aluminum having unsymmetrical metalla- $\beta$ -diketonate ligands. Such complexes can exist as either *cis* ( $C_3$  symmetry) or *trans* ( $C_1$  symmetry) geometrical isomers. Because of the low symmetry of these isomers the PMR spectra are quite complex and peak overlap is extensive. Only the methyl substituent of the chelate ring is a useful probe for isomer identification. The  $^{13}\text{C}$  NMR spectra of XVIII and XIX show much more evidence for this isomerism, and the problem of accidental degeneracy is reduced considerably.

The  $^{13}\text{C}$  NMR spectrum of XVIII consists of 23 resonances. The methyl carbons of the isopropyl group appear as 4 peaks centered at  $\delta$  17.9 ppm. Three of these peaks are assigned to the *trans* isomer where the prochirality of the methyl carbons within each isopropyl group is not observed. The fourth resonance, perhaps the slightly more intense resonance at  $\delta$  17.8 ppm, is assigned to the *cis* isomer.

The methyl carbon atoms of the acetyl fragment appear as 4 peaks, as expected by symmetry, centered at 58.2  $\delta$ . Three peaks are assigned to the *trans* isomer while the slightly larger peak at  $\delta$  58.7 ppm is assigned to the *cis* isomer. A similar assignment is postulated for analogous complexes using PMR data [2,5]. The methine-carbon atoms appear as 3 peaks centered at  $\delta$  65.2 ppm. Although 4 peaks are expected, the resonance at  $\delta$  65.0 ppm is significantly more intense than the other two and probably represents an overlap of the resonance of the *cis* isomer with one of the resonances of the *trans* isomer.

The carbonyl carbon atoms give 4 resonances of nearly equal intensity centered at  $\delta$  191.0 ppm. This asymmetry represents an effective  $C_3$  symmetry for both isomers, and the difference in the environment about each rhenium atom of the *trans* isomer must be very slight.

The acyl carbon atoms appear as 8 resonances as expected by symmetry. These resonances appear as two groups of 4 peaks centered at  $\delta$  302.7 and 306.8 ppm. The peaks centered at  $\delta$  302.7 ppm arise from the acetyl-acyl carbon atoms while the 4 peaks centered at  $\delta$  306.8 ppm are assigned to the acyl carbon atoms of the isobutyryl fragment. Within each group of resonances, three peaks belong to the *trans* isomer and one peak belongs to the *cis* isomer. The two resonances of slightly larger relative intensity at 303.0 and 306.4  $\delta$  are

assigned to the *cis* isomer. Apparently, complex XVIII exists in solution at nearly the statistical distribution of isomers (75% *trans* and 25% *cis*).

The  $^{13}\text{C}$  NMR spectrum of XIX consists of 30 resonances. The methyl carbon atoms appear as three peaks centered at  $\delta$  58.0 ppm. The peak at  $\delta$  57.8 ppm is nearly three times as intense as the other two peaks which may indicate an overlap of the resonance of the *cis* isomer with one of the resonances of the *trans* isomer. A single methylene carbon resonance is observed at  $\delta$  72.4 ppm, but solvent interference apparently obscures other peaks in this region. The phenyl carbon atoms appear as 11 resonances centered at  $\delta$  130.0 ppm and any assignment would be unreliable.

The carbonyl carbon atoms appear as 8 resonances centered at  $\delta$  190.7 ppm. Although the assignment of these peaks is uncertain, we tentatively assign the four resonances of greatest intensity to the *trans* isomer and the remaining four peaks to the *cis* isomer. This relative abundance is consistent with the PMR and the above  $^{13}\text{C}$  data, and the patterns correspond to an effective  $C_3$  symmetry as observed in complex XVIII.

The acyl carbon atoms appear as 7 resonances centered at  $\delta$  300.9 ppm. The peak at  $\delta$  302.0 ppm is twice as intense as the other peaks, and clearly reflects an overlap of two resonances. As observed in the spectrum of XVIII, the acyl carbon resonances establish the presence of both geometrical isomers and provide a quantitative estimate of the relative isomer abundances. A nearly statistical isomer distribution is observed for XIX, also.

## Experimental

All complexes were prepared by known procedures [2–5,15 and 16]. The  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Varian XL-100/Nicolet 1080 Fourier transform NMR spectrometer operating at 25.1400 and 94.0700 MHz, respectively, as  $\text{CDCl}_3$  solutions at 29°C. The  $^2\text{H}$  signal of the solvent was used for locking, and a tilt angle of 90° was used.

For the carbon spectra a repetition rate of 2.3 sec was employed to collect 1500–7000 scans/spectrum. All spectra were  $^1\text{H}$ -decoupled using a 3000 Hz bandwidth. The samples consisted of 0.259–0.706 g of compound and 2.3–5.0 mg of  $\text{Cr}(\text{acac})_3$  dissolved in 4 ml of  $\text{CDCl}_3$  with TMS as internal reference. The samples were not enriched with  $^{13}\text{C}$ . The spectra of acetylacetone,  $\text{Al}(\text{acac})_3$  and  $(\text{acac})\text{BF}_2$  were recorded similarly but without  $\text{Cr}(\text{acac})_3$  and at a repetition rate of 1.3 sec.

For the fluorine spectra a repetition rate of 3.2 sec was employed to collect 20 scans/spectrum. The samples consisted of 0.149–0.769 g of compound and 0.03 ml of  $\text{C}_6\text{F}_6$  dissolved in 4 ml of  $\text{CDCl}_3$ . Chemical shifts were referenced to  $\text{C}_6\text{F}_6$ .

The spectral data for each compound are provided below. The chemical shifts are reported in  $\delta$  (ppm) with respect to the internal reference. Figure 1 shows the  $^{13}\text{C}$  NMR spectra of selected metalla- $\beta$ -diketone derivatives.

$\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_5$  (I):  $\text{CH}_3$  (52.6); CO (broad singlet, 210.0); acyl (255.0).

$\text{CH}_3\text{C}(\text{O})\text{Re}(\text{CO})_5$  (II):  $\text{CH}_3$  (56.7); *trans*-CO (186.0); *cis*-CO (188.0); acyl (252.9).

$(CH_3)_2CHC(O)Re(CO)_5$  (III): CH<sub>3</sub> (17.3); CH (64.7); *trans*-CO (182.2); *cis*-CO (184.5); acyl (254.0).

$C_6H_5CH_2C(O)Re(CO)_5$  (IV): CH<sub>2</sub> (75.5); C<sub>6</sub>H<sub>5</sub> (127.3, 129.3, 130.6, 134.6); *trans*-CO (181.9); *cis*-CO (183.8); acyl (246.6).

Acetylacetonone (V): enol-CH<sub>3</sub> (24.7); keto-CH<sub>3</sub> (30.8); keto-CH<sub>2</sub> (58.6); enol-CH (100.4); enol-acyl (191.9); keto-acyl (202.8). For similar literature values see [17].

$cis-(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)_3]$  (VI): CH<sub>3</sub> (53.5); CO (188.0, 191.1); acyl (297.9).

$cis-(OC)_4Re[C(CH_3)O\cdots H\cdots OCCH(CH_3)_2]$  (VII): CH<sub>3</sub>CH (17.5); CH<sub>3</sub> (53.4); CH (61.3); axial-CO (188.2); equatorial-CO (190.8, 191.5); acetyl-acyl (297.4); isobutyryl-acyl (304.1).

(Acetylacetonate)BF<sub>2</sub> (VIII): CH<sub>3</sub> (24.1); CH (102.1); acyl (193.6).

F (doublet), <sup>23</sup>F, <sup>10</sup>BF and <sup>11</sup>BF). For similar literature values see [17,18].

$[cis-(OC)_4Re(CH_3CO)_2]BF_2$  (IX): CH<sub>3</sub> (53.9); CO (185.6, 189.7); acyl (314.0), F (11.8).

$\{cis-(OC)_4Re(CH_3CO)[(CH_3)_2CHCO]\}BF_2$  (X): CH<sub>3</sub>CH (17.7); CH<sub>3</sub> (53.8); CH (62.7); axial-CO (185.7); equatorial-CO (189.7, 190.1); acetyl-acyl (313.9); isobutyryl-acyl (321.9).

$[cis-(OC)_4Re(CH_3CO)_2]BCl_2$  (XI): CH<sub>3</sub> (54.9); CO (185.4, 189.1); acyl (314.2).

$[cis-(OC)_4Re(CH_3CO)(C_6H_5CH_2CO)]BF_2$  (XII): CH<sub>3</sub> (53.7); CH<sub>2</sub> (70.7); C<sub>6</sub>H<sub>5</sub> (128.4, 129.8, 130.8, 132.6); axial-CO (185.2); equatorial-CO (189.6, 190.0); acetyl-acyl (313.0); phenylacetyl-acyl (314.4).

$[cis-(OC)_4Re(CH_3CO)_2]B(C_6H_5)Cl$  (XIII): CH<sub>3</sub> (54.9); C<sub>6</sub>H<sub>5</sub> (128.6, 128.8, 131.7, 136.3); axial-CO (186.0, 186.4); equatorial-CO (190.0); acyl (310.5).

$\{cis-(OC)_4Re(CH_3CO)[(CH_3)_2CHCO]\}B(C_6H_5)Cl$  (XIV): CH<sub>3</sub>CH (17.8); CH<sub>3</sub> (54.9); CH (63.6); C<sub>6</sub>H<sub>5</sub> (128.4, 128.6, 131.7, 136.1); axial-CO (186.0, 186.2); equatorial-CO (189.7, 190.1); acetyl-acyl (310.0); isobutyryl-acyl (317.7).

(acetylacetonate)<sub>3</sub>Al (XV): CH<sub>3</sub> (26.9); CH (101.3); acyl (192.5). For similar literature values see [17].

$[cis-(OC)_4Mn(CH_3CO)_2]_3Al$  (XVI): CH<sub>3</sub> (54.8); CO (211.9, 217.2); acyl (325.8).

$[cis-(OC)_4Re(CH_3CO)_2]_3Al$  (XVII): CH<sub>3</sub> (58.3); CO (189.9, 191.5); acyl (301).

$\{cis-(OC)_4Re(CH_3CO)[(CH_3)_2CHCO]\}_3Al$  (XVIII): CH<sub>3</sub>CH (17.6, 17.8, 18.0, 18.1); CH<sub>3</sub> (57.8, 58.0, 58.4, 58.7); CH (64.7, 65.0, 65.9); CO (190.1, 190.6, 191.5, 192.0); acetyl-acyl (300.8, 302.3, 303.0, 304.8); isobutyryl-acyl (306.0, 306.4, 306.6, 308.2).

$[cis-(OC)_4Re(CH_3CO)(C_6H_5CH_2CO)]_3Al$  (XIX): CH<sub>3</sub> (57.8, 58.0, 58.3); CH<sub>2</sub> (72.4); C<sub>6</sub>H<sub>5</sub> (127.1, 127.4, 127.6, 128.7, 129.0, 129.4, 130.5, 130.7, 130.8, 134.1, 135.0); CO (188.9, 189.3, 189.7, 191.1, 191.2, 191.7, 191.7, 191.9); acyl (299.3, 299.5, 299.8, 300.7, 301.1, 302.0, 303.6).

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## References

- 1 C.M. Lukehart and J.V. Zeile, *Inorg. Chem.*, in press.
- 2 C.M. Lukehart and J.V. Zeile, *J. Amer. Chem. Soc.*, 99 (1977) 4368.
- 3 C.M. Lukehart and L.T. Warfield, *Inorg. Chem.*, 17 (1978) 201.
- 4 C.M. Lukehart and L.T. Warfield, unpublished results.
- 5 C.M. Lukehart, G.P. Torrence and J.V. Zeile, *Inorg. Chem.*, 15 (1976) 2393.
- 6 C.M. Lukehart and G.P. Torrence, *Chem. Commun.*, in press.
- 7 C.M. Lukehart and J.V. Zeile, *J. Amer. Chem. Soc.*, 98 (1976) 2365.
- 8 C.M. Lukehart, G.P. Torrence and J.V. Zeile, *J. Amer. Chem. Soc.*, 97 (1975) 6903.
- 9 C.M. Lukehart and G.P. Torrence, *Inorg. Chim. Acta*, 22 (1977) 131.
- 10 C.M. Lukehart and G.P. Torrence, *Inorg. Chem.*, 17 (1978) 253.
- 11 O.A. Gansow, A.R. Burke and W.D. Vernon, *J. Amer. Chem. Soc.*, 94 (1972) 2550.
- 12 E.O. Fischer, G. Kreis and F.R. Kreissl, *J. Organometal. Chem.*, 56 (1973) C37.
- 13 W.B. Jennings, *Chem. Rev.*, 75 (1975) 307.
- 14 C.M. Lukehart and G.P. Torrence, *J. Chem. Soc. (Dalton Trans.)*, (1978) 93.
- 15 L.H. Toporcer, R.E. Dessy and S.I.E. Green, *Inorg. Chem.*, 4 (1965) 1649.
- 16 M.L. Morris, R.W. Moshier and R.E. Sievers, *Inorg. Synths.*, 9 (1967) 28.
- 17 J.C. Hammel and J.A.S. Smith, *J. Chem. Soc. (A)*, (1969) 2883.
- 18 N.M.D. Brown and P. Bladon, *J. Chem. Soc. (A)*, (1969) 526.