Journal of Fluorine Chemistry, 20 (1982) 487–496

Received: October 12, 1981

NMR STUDIES OF SOME SECOND AND THIRD ROW TRANSITION METAL COMPLEXES OF MONOTHIO-β-DIKETONES

DANIEL T. HAWORTH* AND MANORANJAN DAS**

*Department of Chemistry, Marquette University, Milwaukee, WI 53233
(U.S.A.)

**School of Chemistry, University of New South Wales, Kensington, N.S.W.
2033 (Australia)

SUMMARY

A ^{13}C and ^{19}F NMR study of twenty-four ruthenium, rhodium, palladium and platinum complexes containing a difluoromethyl or a trifluoromethyl substitutent(R') on the monothio-β-diketone, $RCSCH_2COR'$, is reported. The R-substituents are 2'-thienyl, 2'-naphthyl, phenyl, p-fluorophenyl or p-methylphenyl. The ^{13}C NMR data show the chemical shift of the diketonate ring carbons to be geometry dependent. Similarly, the ^{19}F NMR spectra show chemical shift data which are also metal dependent. The thiocarbonyl and methine carbon's shieldings are also dependent on the nature of the R-group. The rhodium and platinum complexes show carbon-metal and carbon-fluorine spin coupling. The paramagnetic ruthenium(III) complexes give ^{19}F NMR spectral resonances which are broad and shifted upfield from the corresponding diamagnetic rhodium, palladium and platinum complexes. ^{13}C and ^{19}F NMR data supports a *facial* octahedral geometry for the rhodium(III) complexes.

0022-1139/82/0000-0000/$02.75

INTRODUCTION

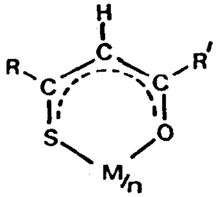
We have recently reported on the results of our carbon-13 and fluorine-19 nuclear magnetic studies of various types of metal chelates of monothio-β-diketones, $RCSCH_2COR'$ [1-4]. These complexes have included metals such as cobalt, nickel, zinc, palladium and platinum and the R-groups have been alkyl, aryl, phenyl and thienyl. The R'-groups have been difluoromethyl, trifluoromethyl and pentafluoroethyl. In general our ^{13}C NMR chemical shift data of the diketonate ring carbons are metal (geometry) dependent. The aryl(phenyl), alkyl and thienyl R-groups also show a chemical shift dependence for the thiocarbonyl and methine carbon resonances. ^{19}F NMR chemical shift data also support a relationship to the geometry of the complex. ^{19}F and ^{13}C NMR data indicate a *facial* octahedral geometry for the cobalt(III) complexes [1-4].

In continuation of our studies on the preparation and characterization of metal monothio-β-diketonate complexes, we now report nuclear magnetic resonance data on a series of metal complexes of $RCSCH_2COCHF_2$ and $RCSCH_2COCF_3$ containing various thienyl, aryl and phenyl R-groups with the metals being ruthenium, rhodium, palladium and platinum. Correlations between the chemical shift of the respective carbon and fluorine resonances with the metal complexed are presented. Spin-spin coupling data for carbon-fluorine, carbon-platinum and carbon-rhodium are also presented.

EXPERIMENTAL

The rhodium and ruthenium complexes were prepared according to the published procedure [5,6], as were the palladium and platinum complexes [7-9].

The NMR spectra were recorded in $CDCl_3$ and were taken on a JEOL-FX60Q NMR Spectrometer. The ^{13}C NMR proton decoupled spectra were run over a 4000Hz sweep width using 16K data points. The complexes of platinum were also accumulated as 8K data points and transformed as 16K data points over a 4000Hz sweep width. ^{19}F NMR spectra were run at 56.3Hz with broad proton decoupling using a sweep width of 15,150Hz. ^{13}C and ^{19}F NMR chemical shifts (ppm) are relative to $(CH_3)_4Si$ and $CFCl_3$, respectively.



RESULTS AND DISCUSSION

Selected ^{13}C NMR chemical shift and coupling constant data for the rhodium complexes are displayed in Table 1. The data show that the carbonyl carbon resonances are mainly affected by the CF_3 group (172.5 ppm) and that the CHF_2 group gave a more deshielded carbonyl carbon resonance at 177.1 ppm. The inductive effect of fluorine is also noted in the chemical shift of the CF_3 carbon (117.3 ppm) as compared to the CHF_2 carbon (110.7 ppm). These shielding results were observed in an earlier study [2]. The thiocarbonyl and methine carbon resonances are R-group dependent with aryl(phenyl) causing more deshielding of these carbon resonances than the 2'-thienyl substitutent. This shielding is also in concert with our previously reported nuclear magnetic resonance data [1-4].

The thiocarbonyl, methine and fluoromethyl carbons show carbon-rhodium coupling and the latter two also show carbon-fluorine coupling. The $^3J_{C-Rh}$ (1.5Hz) coupling constant of the fluoromethyl carbon (R') is clearly

Table 1

^{13}C NMR chemical shift (ppm) and coupling constant (Hz) data for some $Rh(RCSCHCOR')_3$ chelates

R	R'	CS	CO	CH	CF_3/CHF_2	R-Group[a]
$2'-C_{10}H_7$	CF_3	190.5(2.0)[d]	172.5(33.7)[e]	109.6	117.3(283.2)[f]	138.7(1.0)[h]
$2'-C_4H_3S$	CF_3	179.1(2.0)	172.5(33.7)	106.3	117.4(285.4)	144.3(2.0)[h]
$2'-(5'-CH_3C_4H_2S)$[b]	CF_3	178.7(1.5)	171.3(33.7)	105.1	117.4(286.1)	142.1(2.0)[h]
$2'-C_4H_3S$	CHF_2	179.2(1.5)	177.1(23.5)	106.6	110.7(250.1)[g]	144.5(1.5)[h]
C_6H_5	CF_3	190.8(2.0)	172.6(33.4)	109.5	117.3(282.3)	141.4(1.5)[i]
$p-FC_6H_4$	CF_3	188.9(2.0)	172.8(34.2)	109.3	117.3(285.6)	137.4(1.5)[j]
$p-CH_3C_6H_4$[c]	CF_3	190.5(2.0)	172.1(33.7)	108.8	117.4(283.5)	138.7(1.5)[i]

[a] only R-group carbons which show C-Rh spin-spin coupling are shown.

[b] CH_3, 16.0 ppm; [c] CH_3, 21.4 ppm; [d] $^2J_{C-Rh}$; [e] $^2J_{C-F}$; [f] $^1J_{C-F}(CF_3)$; [g] $^1J_{C-F}(CHF_2)$; [h] C-2; [i] C-1

[j] C-1, 137.4(3.4)(1.5); C-2, 128.9(9.3); C-3, 115.6(21.2); C-4, 164.4(253.9).

shown in the two inner resonances of the trifluoromethyl carbon quartet. Spin coupling of rhodium ($^3J_{C-Rh}$) to the quaternary carbon of the R-group is also observed (Table 1). The methine carbon (C-H) showed spin coupling to both fluorine and rhodium to give a quintet of peaks of approximate intensity 1:4:6:4:1. Since $^3J_{C-F}$ is *ca.* 1.5 to 2.0Hz [1-4], then the $^3J_{C-Rh}$ coupling constant must also be of this order to give the apparent quintet of peaks.

The palladium and platinum monothio-β-diketonate complexes show similar shielding trends to the rhodium complexes (Tables 2 and 3). That is, the aryl(phenyl) group gives a larger deshielding of the thiocarbonyl and methine carbons than that of the 2'-thienyl substituent. The platinum compounds also show spin coupling to the C-1($^3J_{C-Pt}$) and C-2($^4J_{C-Pt}$) carbons of the aryl and phenyl groups; to the C-2($^3J_{C-Pt}$) and C-3($^4J_{C-Pt}$) of the 2'-thienyl carbons and to the C-1($^4J_{C-Pt}$), C-2($^3J_{C-Pt}$), C-3($^4J_{C-Pt}$) of the 2'-naphthyl carbons.

The fluorine atom of the p-fluorophenyl group provides an excellent probe for identifying the R-group aryl carbons since all of the metal complexes of p-$FC_6H_4CSCH_2COCF_3$ show carbon-fluorine spin coupling (Tables 1-3). For example, the chemical shifts (ppm) and coupling constants (^nJ,Hz) for the aryl carbons in the rhodium complex are C-1, 137.4(^4J, 3.4); C-2, 128.9(^3J, 9.3); C-3, 115.6(^2J, 21.2) and C-4, 164.4(^1J, 253.9). The palladium and platinum complexes gave similar shielding (±0.3 ppm) and coupling constants (±0.1Hz). The rhodium complexes also show spin-coupling at the C-1 carbon ($^3J_{Rh-C}$, 1.5Hz) and the platinum complexes show ^{13}C-^{195}Pt spin-coupling at the C-1($^3J_{C-Pt}$, 55.9Hz) and C-2($^4J_{C-Pt}$, 8.8Hz) aryl carbons as noted above.

As displayed in Tables 1-3 the octahedral rhodium complexes like the octahedral cobalt complexes give a more deshielded thiocarbonyl and carbonyl carbon than the corresponding carbon in the square planar palladium and

Table 2

^{13}C NMR chemical shift (ppm) and coupling constant (Hz) data of some $Pd(RCSCHCOCF_3)_2$ chelates

R	CS	CO	CH	CF_3	Other
C_6H_5	187.1	171.5(34.2)[a]	110.6(1.5)[b]	117.6(285.2)[c]	
$p-CH_3C_6H_4$	187.0	171.2(33.7)	109.6(1.5)	117.7(285.2)	21.4(methyl)
$2'-C_4H_3S$	175.8	170.9(33.7)	107.4(1.5)	117.6(285.2)	
$p-FC_6H_4$	185.4	171.7(34.2)	110.5(1.5)	117.5(285.2)	(phenyl)[d]
$2'-C_{10}H_7$	186.8	171.4(34.2)	110.7(1.5)	117.7(285.2)	

[a] $^2J_{C-F}(CF_3)$; [b] $^3J_{C-F}(CF_3)$; [c] $^1J_{C-F}(CF_3)$

[d] C-1, 136.8(2.9); C-2 129.1(9.3); C-3, 115.8(22.0); C-4, 164.7(254.4)

Table 3

^{13}C NMR chemical shift (ppm) and coupling constant (Hz) data of some $Pt(RCSCHCOCF_3)_2$ chelates

					R- Group[a]		
R	CS	CO	CH	CF_3	C-1	C-2	C-3
C_6H_5	181.7	165.4(34.2)[c]	112.8(2.0)[d]	119.6(282.7)[e]	141.7(57.6)	126.0(8.3)	
$p\text{-}CH_3C_6H_4$[b]	181.5	165.3(33.7)	112.2(2.0)	118.9(287.6)	139.0(56.6)	126.0(8.8)	
$2'\text{-}C_4H_3S$	170.4	165.1(33.7)	109.6(2.0)	116.3(288.6)		144.9(55.2)	128.2(10.7)
$p\text{-}FC_6H_4$	179.9	165.7(34.2)	112.6(2.0)	119.2(285.0)	(see below)[f,g]		
$2'\text{-}C_{10}H_7$	181.8	165.8(34.6)	113.1(2.0)	118.5(285.2)	126.5(8.8)	139.2(55.2)	123.2(8.4)

[a] only the R-group carbons which exhibit spin-spin coupling to Pt are shown.

[b] 21.5 ppm. CH_3 carbon

[c] $^2J_{C-F}(CF_3)$;[d] $^3J_{C-F}(CF_3)$;[e] $^1J_{C-F}(CF_3)$

[f] C-1, 137.7(3.4)(55.9); C-2, 128.1(9.3)(8.8); C-3, 116.0(22.0); C-4, 164.4(254.4).

[g] first number in parenthesis is $J_{C-F}(p\text{-}FC_6H_4)$, second number in parenthesis is $J(^{13}C\text{-}^{195}Pt)$ for C-1 and C-2.

platinum complexes. Although the differences in the chemical shifts for the respective carbons are greater between the palladium and platinum chelates than the palladium and rhodium chelates the above trend is in agreement with our previous studies [1-4]. The methine carbon's resonance in the square-planar palladium and platinum complexes gave a more deshielded resonance as compared to their octahedral complexes. We have previously shown that tetrahedral zinc monothio-β-diketonate complexes gave the most deshielded C-S carbon resonance [1,2,4]. The order of the chemical shift of the C-S and C-O carbon resonances Zn(II)—tetrahedral>Co(III),Rh(III)-octahedral>Pd(II), Pt(II)-square planar suggest a metal dependence which is geometry related and that oxidation state of the metal is of secondary importance. The R and R' substituents are also a factor in the chemical shift of the diketone carbons as the R' groups such as phenyl or aryl gave a more deshielded C-S carbon resonance as compared to this resonance in the 2'-thienyl or substituted 2'-thienyl R-groups. The inductive effect of the R'-CF_3 group versus the CHF_2 group is seen in the C-O carbon resonances (Table 1). The C-H resonance also shows a R-group dependence with a thienyl substituent giving a more shielded carbon than an aryl (phenyl) group.

The ^{19}F NMR spectral data on these compounds show the metal dependent trifluoromethyl fluorine resonance with the resonances at -74.5, -74.0 and -73.8 ppm for the rhodium, palladium and platinum complexes, respectively. The p-FC_6H_4 fluorine resonance occurred at -107.7 ppm. The corresponding paramagnetic ruthenium complexes of $RCSCH_2COCF_3$(R as in Tables 2 and 3) all gave a broader and more shielded resonances for the CF_3 (-82.0 ppm) and p-FC_6H_4(-110.9 ppm) fluorines than those of the diamagnetic Rh, Pd and Pt complexes.

Our ^{13}C and ^{19}F nuclear magnetic resonance data for the $Rh(RCSCHCOCF_3)_3$ and $Rh(RCSCHCOCHF_2)_3$ complexes all show one resonance for each respective carbon and fluorine atom. These data support a *facial* octahedral geometry for these complexes whereas a *meridional* octahedral geometry would have given three resonances for each type of carbon and fluorine. It is assumed that these compounds are not fluxional and that they have the same stereochemistry in solution and in the solid state. These results are consistent with our ^{13}C NMR data on various tris(monothio-β-diketonate) cobalt complexes [1-4] and with X-ray studies on *facial* octahedral iron(III) and cobalt(III) monothio-β-diketonate complexes [10-11]. Holm has also postulated a *fac*-octahedral structure for some tris(monothio-β-diketonate)cobalt(III) complexes by ^{1}H NMR spectroscopy [12]. Preferential formation of a *facial* octahedral structure is supported by the three sulfur atoms, being at right angles to each other and to the rhodium atom, are able to maximize d_{π}-d_{π} bonding. Also the appreciable values of the dipole moments of the rhodium complexes support a *facial* octahedral configuration [13]. In the same study the dipole moment data for the bis(monothio-β-diketonate) palladium and platinum chelates support a *cis*-square planar geometry [13]. Finally, it is also interesting to note that the rhodium (also the ruthenium) tris(β-diketonate) and tris(acetylcamphorate) complexes are rigid complexes [14] and a partial resolution of the optical isomers of the $Rh(CH_3COCHCOCH_3)_3$ complex has been reported [15].

ACKNOWLEDGEMENTS

DTH gratefully acknowledges support for this work from the Marquette University Committee on Research. We also thank J. W. Beery for assistance in taking the ^{19}F NMR spectra.

REFERENCES

1 M. Das and D. T. Haworth, J. Inorg. Nucl. Chem., 43 (1981) 515.

2 D. T. Haworth, D. L. Maas and M. Das, J. Inorg. Nucl. Chem., 43 (1981) 1807.

3 M. Das and D. T. Haworth, J. Inorg. Nucl. Chem., 43 (1981) 2317.

4 D. T. Haworth and M. Das, J. Inorg. Nucl. Chem., in press.

5 M. Das and S. E. Livingstone, Austra. J. Chem., 27 (1974) 1177.

6 M. Das and S. E. Livingstone, Austral. J. Chem., 27 (1974) 2115.

7 S. E. Livingstone and D. S. Moore, Austral. J. Chem., 29 (1976) 283.

8 M. Das, Transition Met. Chem., 5 (1980) 17.

9 M. Das, S. E. Livingstone, S. W. Filipczuk, J. W. Hayes, and D. V. Radford, J. Chem. Soc. Dalton, (1974) 1409.

10 R. F. Hoskins and C. D. Pannan, Inorg. Nucl. Chem. Lett., 11 (1975) 409.

11 J. Ollis, M. Das, V. J. James, S. E. Livingstone and K. Nimigirawath, Cryst. Struct. Comm., 5 (1976) 679.

12 R. H. Holm, D. H. Gerlach, J. G. Gordon and M. G. McNamee, J. Am. Chem. Soc., 90 (1968) 4184.

13 M. Das, S. E. Livingstone, J. H. Mayfield, D. S. Moore and N. Saha, Austral. J. Chem., 29 (1976) 767.

14 R. H. Holm in L. M. Jackman and F. A. Cotton (Editors), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, Ch. 9, p 347.