CHEMISTRY LETTERS, pp. 1137-1140, 1988.

Diacetonitrilebis(ß-diketonato)ruthenium(II) Complexes. Their Preparation and Use as Intermediates for the Synthesis of Mixed-ligand ß-Diketonato Ruthenium(III) Complexes

Tadashi KOBAYASHI, Yasuhiro NISHINA, Kunio SHIMIZU, and Gen P. SATÔ*
Department of Chemistry, Faculty of Science and Technology, Sophia University,
Kioicho 7-1, Chiyoda-ku, Tokyo 102

Diacetonitrilebis(ß-diketonato)ruthenium(II) complexes were readily prepared by reducing the corresponding tris(ß-diketonato)-ruthenium(III) with zinc amalgam in an acetonitrile—ethanol—water mixture. When a mixed-ligand ß-diketonato complex [RuL$_2$L'] is treated in this way, the more electron-donating ligand is preferentially displaced by two acetonitrile molecules. The diacetonitrile complexes are useful intermediates for the synthesis of mixed-ligand ß-diketonato ruthenium(III) complexes of the type [RuL$_2$L"].

Nitrile complexes of ruthenium(II) have been prepared through substitution of active heteroligands of the parent ruthenium(II) species that are produced by the reduction of the corresponding ruthenium(III) complexes with zinc amalgam or other reductants: $[Ru(NH_3)_5L]^{2+}$ species from $[Ru(NH_3)_5Cl]Cl_2$$^{1)}$ and $[Ru(H_2edta)L_2]$ from K[Ru(Hedta)Cl]$^{2)}$ (L = CH_3CN, C_6H_5CN, etc.). Catalytic hydrogen reduction of tris(ß-diketonato)ruthenium(III) was reported to give diacetonitrilebis(ß-diketonato)ruthenium(II); the acetonitrile ligands of the resulting species could be substituted by more electron-donating ligands, e.g., pyridine; but no details were given.$^{3)}$

This paper presents a simple method for the preparation of diacetonitrile-bis(ß-diketonato)ruthenium(II) complexes. This method is based on the ligand substitution taking place when tris(ß-diketonato)ruthenium(III) is reduced by zinc amalgam in the presence of acetonitrile. The usefulness of diacetonitrile complexes as intermediates is demonstrated by examples.

Table 1. Elemental Analyses

Complex	C(%)		H(%)		N(%)	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Ru^{II}(acac)_2(CH_3CN)_2]$	44.09	43.91	5.29	5.28	7.34	7.08
$[Ru^{II}(tfac)_2(CH_3CN)_2]$	34.36	32.47	2.88	2.69	5.72	5.53
$[Ru^{II}(acac)(hfac)(CH_3CN)_2]$	34.36	34.39	2.88	2.68	5.72	5.67
$[Ru^{III}(acac)_2(dpm)]$	52.27	52.37	6.89	6.90	0.0	0.0
$[Ru^{III}(acac)_2(hfac)]$	35.58	35.44	2.96	2.86	0.0	0.0

The procedure for the synthesis of $[Ru^{II}(acac)_2(CH_3CN)_2]$ ($acac^-$ = acetylacetonate ion) is as follows. Tris(acetylacetonato)ruthenium(III) (0.30 g) was dissolved in a mixture of 100 cm^3 of ethanol, 10 cm^3 of acetonitrile, and 10 cm^3 of water. After 10 cm^3 – 20 cm^3 of zinc amalgam (containing ca. 7 g of zinc shot) was introduced, the mixture was refluxed on a water bath for 2 h. The color of the solution gradually turned from red to orange. The solution was separated by filtration, and then it was evaporated to dryness. When the residue was recrystallized from ethanol, orange crystals were obtained (yield, 0.18 g or 63%). The elemental analyses are listed in Table 1.

This procedure was applicable to other tris(ß-diketonato)ruthenium(III) complexes.[4] For example, $[Ru^{II}(tfac)_2(CH_3CN)_2]$ ($tfac^-$ = 1,1,1-trifluoro-2,4-pentanedionate ion) was synthesized from $[Ru^{III}(tfac)_3]$ in a similar manner (the time for refluxing was 9 h). Brown crystals were obtained on evaporating the water extract of the final residue and then by recrystallizing the solid from aqueous solution (yield, 0.07 g or 27%). The small discrepancies of the elemental analyses of this and the above complex (Table 1) seem to be attributable to the fact that the isolated complexes were not quite stable.

When 0.4 g of $[Ru^{III}(acac)_2(hfac)]$ ($hfac^-$ = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ion) was treated in the same way, a brown residue was obtained. Its silica-gel thin-layer chromatogram (Merck DC-Alufolien Kieselgel 60 F_{254}; developing solvent, ethanol) showed a major, brown spot and a small spot of the unreacted starting material together with a small yellow spot. The yellow substance could not be identified. The brown product was purified chromatographically (Merck Kieselgel 60, 230-400 mesh ASTM; ethanol) and was identified as $[Ru^{II}(acac)(hfac)(CH_3CN)_2]$ (Table 1). This complex was stable and its yield was 0.15 g or 39%. A similar experiment was carried out with a small amount of $[Ru^{III}(acac)_2(dpm)]$ (dpm^- = 2,2,6,6-tetramethyl-3,5-heptanedionate ion). The main product appeared to be $[Ru^{II}(acac)_2(CH_3CN)_2]$, as its IR spectrum was identical with that of the authentic sample except for the presence of four peaks, two of which were attributable to uncoordinated Hdpm. When the crude product was treated with Hhfac as described below, the thin-layer chromatography of the final product indicated that the main component was $[Ru^{III}(acac)_2(hfac)]$ accompanied by small amounts of unidentified impurities.

As shown by these results, this method gives almost exclusively diacetonitrilebis(β-diketonato)ruthenium(II) through displacement of only one β-diketonate ligand of the parent complex; when two kinds of β-diketonates are present, the one which is more electron-donating is preferentially displaced. This is one of the advantages of the present method, along with its simplicity, especially in the case where the diacetonitrile complex is used as an intermediate for preparing a mixed-ligand β-diketonato ruthenium(III) complex.

Diacetonitrilebis(β-diketonato)ruthenium(II) complexes are useful intermediates for the synthesis of mixed-ligand β-diketonato ruthenium(III) complexes, because the acetonitrile ligands can readily be replaced by another β-diketonate ion. The crude diacetonitrile complex contains small amounts of the parent complex and other substances. But these impurities do not interfere with the subsequent operations, and the separation of the diacetonitrile complex is not necessary or rather undesirable, for it tends to lower the yield of the target mixed-ligand complex.

A new compound $[Ru^{III}(acac)_2(dpm)]$ was synthesized from $[Ru^{II}(acac)_2(CH_3CN)_2]$. The crude diacetonitrile complex, prepared according to the above-mentioned procedure from 0.30 g of $[Ru^{III}(acac)_3]$, was dissolved in 100 cm^3 of ethanol. The solution, after the addition of 2 g of Hdpm, was refluxed on a water bath for 1 h and then evaporated to dryness. The solid was dissolved in benzene and subjected to column chromatography (Merck Aluminiumoxid 90, Aktivitätsstufe II - III; benzene). The product was orange crystals (Table 1) and their yield was 0.18 g or 49%. When crude $[Ru^{II}(acac)_2(CH_3CN)_2]$ obtained from 1.00 g of $[Ru^{III}$-

(acac)$_3$] was treated similarly with 5 g of Hhfac, 0.40 g (32%) of [Ru^{III}-(acac)$_2$(hfac)] was finally obtained.

Mixed-ligand β-diketonato ruthenium(III) complexes have been synthesized in other ways. For example, [Ru^{III}(acac)$_2$(hfac)] was prepared by refluxing [Ru^{III}-(hfac)$_3$] with acetylacetone in toluene.$^{5)}$ This method took at least seven days and the yield was small. The "ruthenium blue" method$^{6)}$ is also applicable: a complete series of [Ru^{III}(acac)$_n$(bfa)$_{3-n}$] (bfa$^-$ = 4,4,4-trifluoro-1-phenyl-1,3-butanedione ion) has been prepared.$^{7)}$ This method, however, gives a mixture of the tris and the mixed ligand complexes. Consequently, the individual mixed-ligand complexes have to be isolated chromatographically, and their yields are necessarily small. Use of diacetonitrile complexes is preferable to the use of the "ruthenium blue" method, particularly for preparing complexes of the [RuL$_2$L'] type, because the operations are much simpler and the yields are high.

The authors' thanks are due to Dr. F. S. Howell, Sophia University, for correcting the manuscript.

References

1) R. E. Clarke and P. C. Ford, Inorg. Chem., 9, 227 (1970).
2) A. A. Diamantis and J. V. Dubrawski, Inorg. Chem., 22, 1934 (1983).
3) P. Gandilhon, Ger. Offen. DE 1936727, 29 Jan. 1970, Appl. 19 July 1968.
4) The present method did not work well when the parent tris ruthenium(III) complex had too positive or too negative a value of the standard potential of Ru^{III}/Ru^{II} couple, e.g., [Ru(hfac)$_3$] or [Ru(dpm)$_3$].
5) G. S. Patterson and R. H. Holm, Inorg. Chem., 11, 2285 (1972).
6) A. Endo, K. Shimizu, G. P. Satô, and M. Mukaida, Chem. Lett., 1985, 1984.
7) Y. Hoshino, Y. Yukawa, A. Endo, K. Shimizu, and G. P. Satô, Chem. Lett., 1987, 845.

(Received March 31, 1988)