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The Nitration and Halogenation of Palladium Acetylacetonate*

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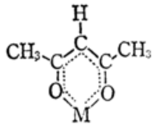
The pseudo-aromatic divalent palladium acetylacetonate has been found to undergo electrophilic substitution at the central carbon of the chelate ring. The mononitro (decomp. p. 240—245°C, λ_{max} 325 mμ) and dinitro (decomp. p. 250—255°C, λ_{max} 324 mμ) palladium acetylacetonates were prepared by treating palladium acetylacetonate with a mixture of copper nitrate trihydrate and acetic anhydride; they were characterized by their infrared and NMR spectra. The halogenation of palladium acetylacetonate was accomplished with *N*-halosuccinimides in chloroform. Dichloro (decomp. p. 205—210°C, λ_{max} 345 mμ), dibromo (decomp. p. 240—245°C, λ_{max} 345 mμ) and diiodo (decomp. p. 195—200°C, λ_{max} 324 mμ) derivatives were isolated and characterized by their spectra.

Recently, a variety of electrophilic substitutions at the central carbon atoms of metal acetylacetonates and related chelate systems have been reported by several authors[1-16]; these substitutions indicate the conspicuous pseudo-aromatic nature of the six-membered rings. By such a process, chloro,[6,13,15] bromo,[6,13] iodo,[6] thiocyano,[7,14] nitro,[4,11,15] acetyl,[4,14] butyryl,[14] benzoyl,[14] formyl,[11] dimethylaminomethyl,[16] chloromethyl,[16] phenylthio[14] and chlorothio[14] groups have been introduced into the stable rings of tris-acetylacetonates of chromium(III), cobalt(III) and rhodium(III).

Previously, Nakamoto, McCarthy and Martell[17] have discussed the relationships between the infrared spectra and the stability of the divalent acetylacetonate; they claimed that the stability of the divalent acetylacetonates decreased in the order of palladium>copper>nickel>cobalt>zinc, and that the stability of the palladium derivative is to be attributed to the exceeding delocalization of the π-electrons as well as of the α-electrons of the metal around all the chelate rings (cf. Fig. 1).



Strong chelate
M=Pd(II)

Fig. 1.

This consideration suggests that palladium acetylacetonate has the pseudo-aromatic structure and may undergo electrophilic substitutions.

This paper will describe the nitration and halogenation of this relatively stable divalent acetylacetonate of palladium. Although palladium acetylacetonate was destroyed by mineral acids, this acetylacetonate was stable in glacial acetic acid. The attempted nitration of palladium acetylacetonate (I) with N_2O_4 in methylene chloride resulted in the destruction of the chelate ring, but a mixture of copper nitrate trihydrate in acetic anhydride proved very effective in the nitration of palladium acetylacetonate (I), and the pure dinitro-chelate (II) was isolated in a high yield by the hydrolysis of the reaction mixtures. The treatment of palladium acetylacetonate (I) with a limited amount of this nitrating agent at 0°C for 4 hr. afforded a 46% yield of mononitro-chelate (III). These nitro-acetylacetonates (II

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[16] R. H. Barker, J. P. Collman and R. L. Marshall, ibid., **29**, 3216 (1964).

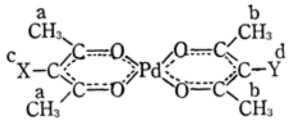
[17] K. Nakamoto, P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

and III) were characterized by analyses and by infrared and nuclear magnetic resonance spectroscopy.

It has been reported that the strong doublet in the 1500—1600 cm^{-1} region of the infrared spectra of metal acetylacetonate is usually united into a singlet by the replacement of the hydrogen at the central carbon by other groups.[6,8,11] On the other hand, the dinitro-chelate (II) exhibits two strong bands in this region. The lower band, at 1525 cm^{-1}, seems to arise from an asymmetric nitro-stretching frequecny. There are no absorption peaks at 1200 cm^{-1} in the spectra of this dinitro-chelate (II). The medium band at 1199 cm^{-1} in the spectra of palladium acetylacetonate (I) has previously been assigned to the bending mode of the hydrogen at the central carbon atom,[17] and Collman et al.[11] have claimed that the absence of this peak is an excellent measure of the complete replacement of metal acetylacetonates at the central carbon.

The proton spin-resonance spectra summarized in Table I provide conclusive proof of the structure assigned to the dinitro-chelate (II). The dinitro-chelate (II) exhibits only one signal, at 7.73τ, whereas the unsubstituted palladium acetylacetonate (I) gives signals at 7.97τ and 4.65τ, with integrated intensities of 6 : 1. The higher field signal (7.97τ) may thus be assigned to the methyl protons, and the lower signal, to the ring hydrogen. The presence of electronegative nitro groups is probably responsible for the shift to a lower field of the methyl proton signal (7.73τ) in the dinitro-chelate (II).

TABLE I. PROTON MAGNETIC RESONANCE SPECTRA AT 60 Mc./sec.



compound	Substituent X	Y	H_a	H_b	H_c	H_d
I	H	H	7.97(6)		—	—
II	NO_2	NO_2	7.73		—	—
III	H	NO_2	7.92(6)	7.75(6)	4.56(1)	—
IV	Cl	NO_2	7.69(1)	7.76(1)	—	—
V	Br	NO_2	7.58(1)	7.75(1)	—	—
VI	Cl	Cl	7.69		—	—
VII	Br	Br	7.55		—	—
VIII	I	I	7.52		—	—

NMR data is presented as τ value and deuteriochloroform was used as solvent.
Relative peak intensities in parentheses.

The structure of the mononitro-chelate (III) was confirmed by its nuclear magnetic resonance spectra (cf. Table I). The mononitro-chelate (III) exhibits proton signals at 7.92, 7.75 and 4.56τ, with relative intensities of 6 : 6 : 1. These signals are assigned to the methyl groups on the unsubstituted ring, the methyl groups on the nitrated ring, and the hydrogen on the unsubstituted chelate ring respectively. A further support for the assigned structure of the mononitro-chelate (III) was obtained from the infrared spectrum. The nitro group gave rise to an asymmetric nitro-stretching frequency at about 1520 cm^{-1}, whereas the appearance of a band at 1200 cm^{-1} indicated the presence of at least one unsubstituted chelate ring. A doublet at 1584 and 1550 cm^{-1} also indicated that not all acetylacetonate rings were substituted at the central carbon.

The structure of the mononitro derivative was further confirmed by the replacement of the other ring by electrophiles. The mixed ligand chelates IV and V were obtained by the chlorination and bromination of the mononitro-chelate (III).

Also, the introduction of halogen into the palladium acetylacetonate ring has been studied. The treatment of a glacial acetic acid solution of palladium acetylacetonate (I) with bromine resulted in the decomposition of the chelate ring. Collman et al.[6] have reported previously that *N*-halosuccinimides are effective halogenating agents for metal acetylacetonates in glacial acetic acid or in chloroform. The treatment of palladium acetylacetonate (I) with *N*-halosuccinimides in chloroform gave dichloro-, dibromo- and diiodo-chelate (VI, VII and VIII respectively) in high yields. These halogenated chelates showed only one signal, at about 7.5 τ, in their nuclear magnetic resonance spectra. The infrared spectra of these chelates (VI, VII and VIII) exhibit a single peak in the 1500—1600 cm^{-1} region and no absorption at 1200 cm^{-1}, providing further evidence of the complete replacement of all chelate rings at the central carbon.

Experimental[18]

Palladium Acetylacetonate (I).—This compound was prepared by the procedure of Grinberg.[19]

Bis(3-nitro-2, 4-pentanediono)-palladium (II). — A mixture of 2.4 g. (10 mmol.) of copper nitrate trihydrate and 70 ml. of acetic anhydride was stirred for 45 min. at 0°C. At the end of this time, a portion of the copper nitrate had been dissolved to form a deep blue solution. To this solution there was then added one gram (3.3 mmol.) of palladium acetylacetonate (I), and the resulting mixture was stirred for 4 hr. at 0°C, and then for one more hr. at room temperature.

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[18] All melting points are uncorrected. The infrared spectra were measured in KBr disks with a Hitachi EPS-2 infrared spectrometer, while the ultraviolet absorption spectra were measured in a chloroform solution with a Hitachi recording spectrophotometer, model EPU-2.

[19] A. A. Grinberg and I. Simonova, *Zhur. Priklad. Khim.*, **26**, 880 (1953); *Chem. Abstr.*, **47**, 11060 (1953).

The solution was decomposed by stirring it for two hr. with 500 ml. of 1 : 1 ice-water which had been buffered with 10 g. of sodium acetate. The fine pale yellow precipitate was collected on a filter, washed with water, and then recrystallized from benzene. The yield of bis(3-nitro-2, 4-pentanediono)-palladium (II) was 0.97 g. (72%). It darkened from about 220°C and decomposed at 250—255°C. IR spectrum (KBr): 1581, 1525 (NO_2), 1468, 1420, 1346, 1102, 932, 826 (NO_2) and 702 cm^{-1}; UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 324 (3.95).

Found: C, 30.46; H, 3.01; N, 6.85. Calcd. for $C_{10}H_{12}O_8N_2Pd$: C, 30.45; H, 3.06; N, 7.09%.

(2, 4-Pentanediono) - (3 - nitro-2, 4-pentanediono)-palladium (III).—A mixture of 0.79 g. (3.3 mmol.) of copper nitrate trihydrate and 20 ml. of acetic anhydride was stirred for 45 min. at 0°C. To this solution there was then added one gram (3.3 mmol.) of palladium acetylacetonate (I). The resulting mixture was stirred for 4 hr. at 0°C, allowed to come to room temperature, and then stirred for one more hour. The reaction mixture was poured into a mixture of 100 g. of ice, 100 ml. of water, and 5 g. of sodium acetate, and then stirred for one hour. The water layer was extracted three times with chloroform, and the combined chloroform extracts were washed with a 5% aqueous sodium bicarbonate solution and then water. After solution had been dried over sodium sulfate, the solvent was removed under a vacuum. The resulting yellow residue was purified by recrystallization from benzene and obtained in a 46% yield (0.65 g.). It darkened at about 190°C and decomposed at 240—245°C. The purity of this product was checked by the chromatography of a small portion on alumina, using chloroform as the eluent. IR spectrum (KBr): 1584, 1550, 1520 (NO_2), 1475, 1370, 1345, 1200 (C–H bending), 1078, 823 (NO_2) and 745 cm.$^{-1}$. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 325 (396).

Found: C, 34.95; H, 3.91; N, 4.12. Calcd. for $C_{10}H_{13}O_6NPd$: C, 34.35; H, 3.75; N, 4.00%.

Bis(3-chloro-2, 4-pentanediono)-palladium (VI).—A solution of 600 mg. (2.0 mmol.) of palladium acetylacetonate (I) and 1.06 g. (8.0 mmol.) of *N*-chlorosuccinimide in 50 ml. of chloroform was heated at reflux for 20 min., washed with a 5% aqueous sodium sulfite solution, and then washed with water. After the organic layer had been dried over sodium sulfate, the solvent was removed under a vacuum. The residue was recrystallized from benzene, and 580 mg. (77%) of bis(3-chloro-2, 4-pentanediono)-palladium (VI), m. p. 205—210°C (decomp.), was obtained. IR spectrum (KBr): 1550, 1452, 1367, 1041, 928 and 690 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 345 (4.09).

Found: C, 32.19; H, 3.38; Cl, 18.64. Calcd. for $C_{10}H_{12}O_4Cl_2Pd$: C, 32.13; H, 3.21; Cl, 19.01%.

Bis(3-bromo-2, 4-pentanediono)-palladium (VII).—A mixture of *N*-bromo-succinimide (1.424 g., 8.0 mmol.) and palladium acetylacetonate (I) (600 mg., 2.0 mmol.) in 50 ml. of chloroform was boiled for ten minutes, washed with an aqueous sodium sulfite solution, and then washed with water. The chloroform solution was dried over sodium sulfate, the chloroform was removed, and the resulting solid was recrystallized from benzene. The yield of bis(3-bromo-2, 4-pentanediono)-palladium was 630 mg. (68%). It decomposed at 240—245°C. IR spectrum (KBr): 1545, 1445, 1347, 1025, 927 and 694 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 345 (3.94).

Found: C, 26.10; H, 2.81; Br, 33.92. Calcd. for $C_{10}H_{12}O_4Br_2Pd$: C, 25.97; H, 2.61; Br, 34.63%.

Bis(3-iodo-2, 4-pentanediono)-palladium (VIII).—A mixture of *N*-iodo-succinimide (1.8 g., 8.0 mmol.) and palladium acetylacetonate (600 mg., 2.0 mmol.) in 70 ml. of chloroform was stirred at room temperature for one hour, washed with an aqueous sodium bisulfite solution, and then washed with water. After the chloroform solution had been dried, the solvent was removed under a vacuum and the resulting solid was recrystallized from benzene. Yellow crystals (650 mg., 60%) of bis-(3-iodo-2, 4-pentanediono)-palladium were obtained. They decomposed at 195—200°C. IR spectrum (KBr): 1548, 1445, 1351, 1025, 927 and 691 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 324 (3.84).

Found: C, 21.13; H, 1.87; I, 45.62. Calcd. for $C_{10}H_{12}O_4I_2Pd$: C, 21.97; H, 2.19; I, 46.51%.

(3-Chloro-2, 4 - pentanediono)(3 - nitro - 2, 4-pentanediono)-palladium (IV).—This compound was prepared from (2, 4-pentanediono)(3-nitro-2, 4-pentanediono)-palladium (III) and *N*-chloro-succinimide in chloroform by the usual manner (70% yield). The yellow crystals darkened at 193—198°C and decomposed at 230°C. IR spectrum (KBr): 1523 (NO_2), 823 (NO_2) and no peak at 1200 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 325 (4.08).

Found: C, 30.41; H, 2.96; N, 3.47. Calcd. for $C_{10}H_{12}O_6NClPd$: C, 31.25, H, 3.12; N, 3.62%.

(3 - Bromo - 2, 4 - pentanediono) (3 - nitro-2, 4-pentanediono)-palladium (V).—This compound was prepared from mononitro-chelate (III) and *N*-bromo-succinimide in chloroform by the usual manner (75% yield). It darkened at 190—195°C and decomposed at 220—225°C. IR spectrum (KBr): 1524 (NO_2), 826 (NO_2) and no peak at 1200 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} mμ (log ε) 235 (4.11).

Found: C, 28.55; H, 3.01; N, 3.37. Calcd. for $C_{10}H_{12}O_6NBrPd$: C, 28.03; H, 2.80; N, 3.27%.

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